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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. A. F. CASTLE is home from Iraq.
Count HENRI M. DE CIZANCOURT has left Madagascar and is in France.
Mr. J. J. G. CLARK is in Rumania.
Mr. L. O. DALTON is in Peru.
Mr. T. R. H. GARRETT is home from Java.
Mr. W. KOHRING has left for Persia.
Mr. S. O. NEWTON is home from Persia.
Dr. SIMON PAPP has left Hungary and is in England.
Mr. J. S. PARKER is in Egypt.
Mr. J. D. SHACKLETON is home from Burma.
Mr. E. R. TIDEY has returned to Mexico.

The Secretary would be glad to hear of the whereabouts of the following members :—C. A. BAUDUIN, A. E. O. COOKE, W. M. GRAY, W. J. HARRIS, L. B. HOLLOWAY, C. E. JOBLING, A. F. C. PARKER, NAND LAL PASI, W. W. SCOTT, W. E. SHEPHERD, R. K. VAN SICKLE and F. E. G. WATSON.

DINNER CLUB.

The attention of members is drawn to the Dinner Club of the Institution. This Club holds informal dinners after each General Meeting of the Institution and members may invite guests. Those desiring to receive notice of these dinners, are requested to inform the Secretary of the Institution.

OBITUARY.

GEORGE JOHNSTON.

We regret to announce the death of Mr. George Johnston, which occurred in a nursing home at Edinburgh on November 1st, 1930.

Born in 1874, Mr. Johnston was educated at Muray House Training College, Edinburgh, and then went to the Heriot Watt College, Edinburgh. He was apprenticed for five years at Messrs. Bertrams, Ltd., Engineers, Edinburgh, and then served for twelve months as a sea-going engineer with the Anchor Line Steamship Company.

From 1898 to 1901 he was employed by the Sierra Leone Government on railway construction work in that colony, and from 1901 to 1906 was engaged on marine engineering and construction with Messrs. D. and W. Henderson, at Glasgow.

In 1908 he went to Persia for the Anglo-Persian Oil Company, and in 1911 was employed in Mexico as Driller and Production Superintendent by the Mexican Petroleum Company. In 1914 he was engaged by the La Corona Petroleum Maatschappij as Field and Construction Superintendent in Mexico, and in 1920 was appointed Manager to the Caltex Oil Company of Mexico.

In 1921 he was appointed Field Superintendent to the Oilfields of England, Ltd., at Kelham, Nottingham, and latterly spent five years in Venezuela with the Lago Petroleum Company.

He leaves a widow and two sons, and to them we tender our sincere sympathy in their great loss.

NOMINATIONS FOR MEMBERSHIP OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The following have been nominated for membership of the Institution of Petroleum Technologists and their Application Forms may be seen at the Offices of the Institution :—

As Members.—Robert Illtyd Lewis, Arthur Richard Pattisson, Jack Francis Mahon Taylor, Sijbren Timjstra.

As Transfer to Member.—Mostafa Allam.

As Associate Members.—William Lawrence Bouch, Richard Godfrey, Vacey Vivian Linnington Hope, Herbert Leonard Joseph Hunter, Eric Rofe Styles, Alfred Reginald Thomas.

As Transfer to Associate Members.—Norman Macdonald Brodie, Kenneth Brebner Ross, Geoffrey Stuart Taitt.

As Students.—Michael Abramovitch, Geoffrey Melvin Barrett, Arthur Evans, Percival George Higgs, Giles Philip Elliot Howard, Hugh John Marks, Leslie Benjamin Sweetland, William Roy Wright.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND THIRTIETH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, London, on Tuesday, November 11th, 1930, the chair being taken by Prof. J. S. S. Brame, C.B.E. (Past-President).

The Secretary read the names of members elected and candidates nominated for election as follows :—

The following were elected on October 31st, 1930 :—

As Transference to Members.—Francis Roger Spencer Henson, Niels Matheson.

As Associate Members.—George Barclay, David Neill McKinlay, Kenneth Arthur Spearing, Arthur Augustus Weir.

As Transference to Associate Member.—Donald Thomas Jones.

As Student.—Willem Jan Hessels.

The following were nominated on September 3rd, 1930 :—

As Members.—William Ernest Victor Abraham, George Calzavara, Andre Graetz, George Hulme Hubbard, Theodore Alaric Peck, Francis Martin Potter.

As Transference to Members.—Albert Harold Seagrim, Henry N. L. C. E. C. de Wilde.

As Associate Members.—Jean Georges Berteloot, Max Capper, Eric Carter, Stanley Owen Connor, Norman Russell Fowler, Donald George Hitt, Thomas Reginald Palmer, Robert George Perry, Walter Sigg, Colin McLuckie White.

As Transference to Associate Members.—Maurits Julius Bernard de Blank, Douglas Johnathan Pull, Jesse Ossowa Tanner.

As Associates.—Douglas Oliver Bremner, George Norton Critchley, Alexander P. Shearer, Thomas Gilbert Webb.

The following were nominated on October 14th, 1930 :—

As Member.—Robert Webb Farmborough.

As Associate Members.—George Philip Bowring, Leslie Vincent Woodhouse Clark, (Miss) Winifred Sarah Elizabeth Clarke, Noel William Grey, Ernest Noel Hague, Arthur Noel Lucie-Smith.

As Transference to Associate Member.—George Dickinson.

As Students.—John George Beastall, Richard Vernon Browne, John Leslie Howard, Geoffrey Howard Hunter-Brown, John Alexander Pryde, Tadeusz Rudolf Rogala.

As Associate.—Roland Doumin.

The following were nominated on November 11th, 1930 :—

As Members.—Percy George Hamnall Boswell, Ionel I. Gardescu, William Ladislas Gomory, Eric Stanley Hillman, Edward Alfred Hunting, Arthur John Wright.

As Associate Members.—Roland Edwards Hales, Harold Leslie Lyne, James Ness Rodger.

As Transference to Associate Member.—Herbert Richard Lovely.

As Student.—Laurence George Melville Roberts.

As Associates.—Thomas Moore Hickman, John Arthur Reed Pepper.

The Chairman said that as the President was away in the United States the pleasant duty of taking the Chair at that meeting, at which Prof. A. W. Nash was to deliver a paper on Synthetic Lubricating Oils, fell to his lot, and he had great pleasure in calling upon the Professor to deliver his address.

The following paper was then read by Prof. A. W. Nash :—

Synthetic Lubricating Oils.

A report of some experiments carried out on ethylene for the production of light and heavy oils, including the examination of the lubricating oil fractions and remarks on the oiliness factor of lubricants generally.

By Prof. A. W. Nash, M.Sc., F.C.S., M.I.Mech.E. (Member), H. M. Stanley, M.Sc., and A. R. Bowen, M.Sc., Ph.D., F.I.C. (Associate Members).

Ethylene has long been known to yield polymerisation products which have been described from time to time as light or heavy oils. Very little investigation has been made, however, regarding the value of the synthetic oils boiling in the lubricating range, when compared with petroleum lubricants of the same viscosity and physical characteristics. The olefine, ethylene, can be made to polymerise under such influences as: (*a*) ultra-violet light; (*b*) silent electric discharge; (*c*) heat; (*d*) pressure; (*e*) catalysts, or by combination of these. The oils to be described in this paper were produced by the last three of these influences. For a full account of the chemical reactions involved in the polymerisation of ethylene and the work of previous investigators a recent publication by one of us should be consulted.[1]

Briefly the polymerisation reaction can be visualised by considering the simplest step, namely, the polymerisation to butylene, a reaction which has recently been covered by a patent.[2]

$$\begin{matrix} CH_2 \\ \| \\ HCH \end{matrix} + H_2C = CH_2 \xrightarrow[\text{Catalyst}]{AlCl_3} \begin{matrix} CH_2 \\ \| \\ HC—CH_2—CH_3 \end{matrix}$$

In order to effect the simple polymerisation, where only two molecules of ethylene combine together, the reaction must be arrested within a short time of commencement. In the usual way the polymerisation tends to go much further, involving many molecules of ethylene, and oils are obtained which contain *all fractions from gasoline to heavy lubricating oil in range.*

Catalysts such as aluminium chloride and boron trifluoride greatly facilitate rapid polymerisation and their action, especially that of aluminium chloride, is well analysed in the above-mentioned paper. In the case of the latter catalyst the polymerisation reaction is in all probability one of the Friedel-Crafts type. Thus complex aluminium chloride-hydrocarbon compounds would be expected, and these were actually isolated during the experiments. When these complex compounds are decomposed by water, unsaturated oils of olefinic type are liberated.

The oils to be described in this paper are the products of some of the experiments in which ethylene was polymerised by heating in an autoclave up to 60 atm. pressure with and without the aid of catalysts.

In the absence of any catalyst, ethylene under pressure did not polymerise in the autoclave used until 325° C., this polymerisation being very rapid at 350° C. This temperature was lowered by the use of zinc chloride catalysts (230–275°), while stannic chloride and titanium tetrachloride produced only negligible quantities of liquid products at temperatures up to 100°. The case of aluminium chloride as a catalyst was given the most consideration in this work on account of its pronounced action, both at ordinary temperature and at temperatures up to 180° C. At ordinary temperatures the products were of two types: (1) a free oil, and (2) a double compound of aluminium chloride and liquid hydrocarbons, from which the combined oil was extracted by decomposition with iced water.

The free oil consisted of liquid hydrocarbons, mostly of a saturated nature containing from about 10 to 45 carbon atoms in their molecules. The lower boiling fractions contained proportions of paraffin hydrocarbons, but the main part of the oil consisted of saturated compounds, presumably cyclo-paraffins.

The combined oil, liberated from the pasty aluminium chloride additive compounds, also consisted of a complex mixture of hydrocarbons with from 10 to more than 50 carbon atoms per molecule. These hydrocarbons were unsaturated and are probably to be regarded as composed of hydrocarbons of the olefine series of the formula C_nH_{2n}, admixed with hydrocarbons of lower hydrogen content (probably unsaturated cyclic hydrocarbons).

At higher temperatures the polymerisation of ethylene under pressure in the presence of aluminium chloride was much more rapid, but the life of the catalyst was considerably curtailed. As before, free oil and aluminium chloride double compounds were formed, but these differed considerably from the products obtained at lower temperatures. The aluminium chloride complex tended to become more and more carbonaceous as the temperature was increased, and above 100 to 150° C. it was not possible to obtain oil from this material at all, but only a relatively small amount of a heavy black tar.

The free oil produced at higher temperatures was a pale yellow, clear oil, containing large proportions of low-boiling constituents in contrast to the viscous free oil produced at lower temperatures. The low boiling fractions consisted of paraffin hydrocarbons from pentane upwards, whilst the higher boiling fractions were deficient in hydrogen and corresponded to the formulæ C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}. These latter substances probably belong to the class of polynuclear naphthenes. At higher temperatures lower paraffin hydrocarbons appeared in the residual gases from the experiments, their amount increasing with rise in temperature.

Briefly, it is believed that the formation of the numerous products by the action of aluminium chloride can be explained on the basis of three well-known reactions, namely: (1) polymerisation of ethylene to higher olefines; (2) isomerisation of these olefines to produce the corresponding cyclo-paraffins; and (3) cracking of the latter under the influence of aluminium chloride to produce light paraffin hydrocarbons and heavy oils less rich in hydrogen.

The various distillates obtained from oils produced by the action of aluminium chloride on ethylene under pressure at ordinary temperature and at 150° C. have been carefully examined. Their densities, refractive indices, molecular weights, and in many cases their elementary analyses have been determined. In particular, the higher boiling fractions, having viscosities of the same order as those of commercial lubricants, have been studied, and mechanical tests have been carried out with a view to determining their possible value as synthetic lubricants.

The caution needed in the interpretation of the results obtained from friction testing machines and the relative value of such tests are well-known to the Authors.

Experimental.

The autoclaves used included the 2-litre bomb previously described in connection with hydrogenation of coal experiments[3], and a similar rotating, gas-heated type of half a litre capacity. In later experiments a glass lining was introduced where catalysts might have a corrosive action on the walls of the autoclaves.

Substantially pure ethylene (containing, as sole impurity, small amounts of hydrogen), compressed in cylinders under 60–70 atm. pressure was used for these experiments. Gas analyses were carried out on the Bone and Wheeler modified apparatus[4], and the Tropsch-Dittrich apparatus[81] was employed for the condensation analyses of gaseous hydrocarbon mixtures.

All temperatures recorded in this paper refer to Centigrade scale.

Polymerisation of Ethylene without Catalysts.—In the absence of added catalytic material ethylene is stable under pressure at temperatures up to about 300°. At 325° a gradual decrease of pressure took place, and with increasing temperature the condensation became more rapid. Thus on heating ethylene (initial pressure 51 atm. at 20° and 135 atm. at 340–350°) for 7 hours in the small steel autoclave, the pressure fell uniformly from 140 to 32 atm. When cold the pressure was 7 atm., and the gaseous product of the reaction was 4·3 litres of a gas of the composition :—

$$C_2H_4\ 68{\cdot}1\%\ ;\ \text{higher olefines}\ 7{\cdot}4\%\ ;\ H_2\ 0{\cdot}6\%\ ;\ C_nH_{2n+2\ (n=2\text{-}0)}\ 23{\cdot}8\%.$$

The liquid reaction product (28·3 gm.) was of a yellow colour with slight fluorescence, and on distillation gave the following fractions and percentages by weight : I.B.P. 45°/750 mm. ; Fraction (1) 45°–100°/750 mm., 17% ; Fr. (2) 100°–200°/750 mm., 35% ; Fr. (3) 200°/750 mm.–200°/13 mm., 36% ; Fr. (4) above 200°/13mm., 12%. The first two fractions were almost colourless, while (3) and (4) were yellow and brownish yellow respectively.

Polymerisation of Ethylene under Pressure in the Presence of Aluminium Chloride at Ordinary Temperatures.—When ethylene was introduced under pressure into the autoclave in the presence of powdered aluminium chloride *at ordinary temperature*, a very gradual decrease in pressure indicated that polymerisation was taking place, and on opening the autoclave a yellow viscous oil was found to have been formed. At the same time a large part of the aluminium chloride had been converted into what was apparently a double compound with hydrocarbons.

In order to effect this reaction, freshly-sublimed aluminium chloride was found to be most suitable. Samples of aluminium chloride which had been stored for some time were almost inactive in promoting this reaction. Furthermore it is advantageous that the aluminium chloride be very finely powdered.

It was further noticed that the presence of a diluent liquid, such as petroleum ether, was favourable to the process of polymerisation. This is to be explained, probably, on the basis of the increased contact between the ethylene and the aluminium chloride owing to better agitation and also due to the great solubility of ethylene

under pressure in the liquid diluent. The use of petroleum ether has been previously mentioned as part of the well-known Allenet process.

Low boiling aromatic-free petroleum ether was employed in most of the experiments with aluminium chloride for several reasons. Since the actual products of polymerisation were high boiling the separation of liquid diluent and polymerisation product was easily accomplished. It was found, also, that if aromatic hydrocarbons were present, combination of ethylene with the aromatic hydrocarbon took place with the production of ethylated substances; thus with benzene the product of the action of ethylene in the presence of aluminium chloride was a solid hydrocarbon of M.P.129° which was found to be hexaethyl-benzene. Therefore, in order to avoid such complications, the absence of aromatic hydrocarbons from the diluent must be assured. Finally the use of low boiling petroleum ether is to be preferred, since aluminium chloride has practically no action upon this liquid at temperatures below 100°.

In some of the experiments the liquid diluent was saturated with dry hydrogen chloride gas, but no beneficial results followed the use of this material so far as could be judged from the yields of products.

Operating at low temperatures (0°–20°) with finely divided aluminium chloride, the products were found to consist of (1) *an uncombined oil* (designated " A " in the following) and (2) a double compound of aluminium chloride and hydrocarbons from which the *combined oil* (designated " B " oil in the following account) could be extracted after decomposition with water. These two types of oils " A " and " B " were of such different characters that they were always recovered and examined separately.

The following methods were accordingly adopted for dealing with crude products found in the autoclave. The free oil was extracted by washing the reaction product many times with dry aromatic-free petroleum ether (boiling range 60°–80°); the extract was then washed with alkali, dried and distilled to remove the petroleum ether. The residual double compound was decomposed very cautiously with iced-water and the liberated oil extracted with benzene. The extract was washed several times with alkali, thoroughly dried, and distilled to remove the volatile solvent. The oil A and the oil B were then distilled separately under 10 mm. of mercury pressure and the distillates examined. The distillates of the " A " series were colourless oils having low bromine values when examined by the Francis method, while the distillates of the " B " series were darker in colour and showed rather high bromine and iodine values.

Experiment 34 was carried out in the larger (2 litre) autoclave, the charge being 100 gm. of aluminium chloride and 100 gm. of aromatic-free petroleum ether (60°–80°). The experiment lasted 23 days, ethylene being recharged into the autoclave daily, the average temperature being 5° to 10°, and the autoclave was rotated most of the time. The average pressure of ethylene was 35–40 atm., the maximum pressure being 55 atm. In the first few days of the experiment the pressure reduction was about 15 atm. per day, but later this fell to below 10 atm. per day. At the end of the experiment the residual gas contained only ethylene and a little hydrogen. The products were worked up as stated previously and consisted of :—

219 gm. of free oil (A).
68 gm. of combined oil (B).

Distillation of these two oils under 10 mm. pressure in a vacuum distillation apparatus gave the following distillates :—

Distillation of Oil from Experiment 34.

Boiling range. °C.	Free oil. Fraction.	Free oil. Wt. in gm.	Free oil. %	Combined oil. Fraction.	Combined oil. Wt. in gm.	Combined oil. %
Up to 100°/10 mm.	1A	38·0	17·4	1B	9·7	14·4
100°–150°/10 mm.	2A	37·5	17·1	2B	8·3	12·3
150°–200°/10 mm.	3A	25·5	11·6	3B	10·1	15·0
200°–250°/10 mm.	4A	30·7	14·0	4B	8·3	12·3
Above 250°/10 mm.	5A	87·3	39·9	5B	31·1	46·0
Total ..	—	219·0	100·0	—	67·5	100·0

The above distillates were examined in some detail, and the bromine values and elementary analyses are given below.

Characteristics of Distillates. Experiment 34.

Fraction.	D^{20}_4	Bromine number* (Francis).		% C.	% H.	
1A ..	0·7581 ..	0·9	0·9 ..			
2A ..	0·7843 ..	2·6	2·6 ..			
3A ..	0·8068 ..	3·6	3·7 ..	85·00 ..	14·77	
4A ..	0·8227 ..	6·0	5·9 ..	84·99 ..	14·61	C_nH_{2n}
5A ..	— ..	7·1	7·0 ..	85·36 ..	14·30	requires
1B ..	0·7735 ..	21·2	18·0 ..	— ..	—	C=85·62%
2B ..	0·8107 ..	23·4	27·7 ..	85·43 ..	13·96	H=14·38%
3B ..	0·8388 ..	33·0	38·0 ..	85·50 ..	13·80	
4B ..	0·8517 ..	37·0	32·6 ..	86·08 ..	13·82	
5B ..	— ..	33·4	40·0 ..	85·94 ..	13·79	

* Gm. of bromine per 100 gm. of oil.

It appears from the analyses that both the "A" and "B" oils approximate to the formula C_nH_{2n}: however the lower fractions of the "A" series are richer in hydrogen while the "B" series are somewhat more deficient in hydrogen than is indicated by this formula.

Experiment 45–50.—A series of experiments was made in the large autoclave to test the effect of time on the character of yields of the products. The experiments were all carried out at about 10° to 15° and the charge in the autoclave in each case was 100 gm. of finely powdered fresh aluminium chloride and 50 gm. of aromatic-free petroleum ether (60°–80°). The initial pressure of ethylene was usually 50–55 atm., the average pressure throughout the experiments being about 40 atm., the autoclave being recharged daily with ethylene as before. The following table shows the yields of "free" and "combined" oil ("A" and "B" series) after various periods of time, and for the sake of comparison the yields obtained in Experiment 34, previously described, are included.

			Free oil A.			Combined oil B.		
Expt.	Duration in hours.	Atm. of C_2H_4 absorbed.	Wt. in gm.	D^{20}_4	Bromine number (Francis).	Wt. in gm.	D^{20}_4	Bromine number (Francis).
45	46	47	114	0·8057	—	50	0·8449	—
46	47	47	122	0·8057	3·8	49	0·8546	34
47	70	83	127	0·8087	4·4	80	0·8459	20
48	95	—	130	0·8081	—	65	0·8505	—
49	95	—	138	0·8048	—	65	0·8552	—
50	143	97	156	0·8100	3·7	60	0·8659	37
34	550	200	219	—	—	68	—	—

From the results reproduced in the above table the following important points are noteworthy. (1) Whereas the yield of the "A" oils ("free oils") increases with increase in the duration of the experiment, the yield of the combined ("B") oils is very nearly constant and seems to be independent of the duration of the experiment. This conclusion is very important when considering the theory of the process as discussed in the introduction of this paper. (2) The densities of both the "A" and "B" series of oils increase slowly with increase in the duration of the experiment indicating that the polymerisation process is of a cumulative nature.

The oils obtained from Experiments 45–50, amounting in all to 907 gm. of the "free" oil and 310 gm. of "combined" oil, were carefully distilled under a constant pressure of 10 mm. of mercury absolute, the results of this distillation being tabulated in the following table.

Boiling range. °C.	Free oil A. Fraction.	Wt. in gm.	% of total.	Combined oil B. Fraction.	Wt. in gm.	% of total.
Up to 100°/10 mm. ..	1A	173	19·1	1B	37·3	12·0
100°–125°/10 mm. ..	2A	83	9·1	2B	13·8	4·5
125°–150°/10 mm. ..	3A	85	9·4	3B	20·7	6·7
150°–175°/10 mm. ..	4A	85	9·4	4B	22·7	7·3
175°–200°/10 mm. ..	5A	87	9·6	5B	34·0	11·0
200°–225°/10 mm. ..	6A	66	7·3	6B	30·0	9·7
225°–250°/10 mm. ..	7A	61	6·7	7B	31·3	10·1
Above 250°/10 mm. .	8A	267	29·4	8B	120·0	38·7
Total		907	100·0		309·8	100·0

The properties of the various distillates of both the "A" and "B" series of oils from Experiments 45–50 are tabulated below. The refractive indices were determined by means of an Abbe refractometer while the molecular weights were determined in benzene solution by means of the cryoscopic method. Since it is known that the molecular weights of some oils in benzene solution vary with the concentration, an amount of solute was used to give approximately the same depression of the freezing point throughout ($\Delta F=0.5°$). Several results by the ebullioscopic method in benzene confirmed the cryoscopic results.

Properties of Distilled Oils from Experiments 45–50.

Fraction.	D^{20}_4	N^{20}_D	Mol. Wt.	Bromine number (Francis).	Elementary analyses. % C.	% H.	Approx. formula.
1A	0·7517	1·4207	152	—	84·39	14·95	$C_{11}H_{22}$ and $C_{11}H_{24}$
2A	0·7807	1·4350	210	1·3	84·86	14·93	$C_{15}H_{30}$ and $C_{15}H_{32}$
3A	0·7942	1·4448	244	—	84·96	14·80	$C_{17}H_{34}$ and $C_{17}H_{36}$
4A	0·8052	1·4499	272	2·8	85·03	14·61	$C_{20}H_{40}$
5A	0·8160	1·4555	309	—	85·03	14·75	$C_{22}H_{44}$
6A	0·8249	1·4594	357	4·4	85·26	14·57	$C_{25}H_{50}$
7A	0·8332	1·4622	384	—	85·20	14·51	$C_{28}H_{56}$
8A	—	1·4721	591	6·9	85·36	14·35	$C_{42}H_{84}$
1B	0·7521	1·4267	133	30, 36	84·88	14·63	C_nH_{2n} requires
2B	0·8200	1·4649	198	38, 44	86·11	13·48	C = 85·62%
3B	0·8357	1·4735	228	37, 32	86·01	13·31	H = 14·38%
4B	0·8451	1·4795	262	35, 40	86·07	13·33	
5B	0·8526	1·4823	305	44	86·17	13·41	
6B	0·8584	1·4848	344	46	86·27	13·31	
7B	0·8636	1·4863	380	32	86·19	13·42	
8B	—	—	729	28	86·07	13·33	

Microchemical analysis showed the fractions to be free from chlorine except fraction 6B which contained 0·2 per cent.

Since the viscosities of the higher boiling fractions were of great interest, both from the point of view of their possible use as lubricating oils and also from a theoretical standpoint, the viscosities of fractions 5A, 6A, 7A, 5B, 6B and 7B were determined at 20°,

50° and 80°, using B.E.S.A. Ostwald viscometer tubes, which had been carefully calibrated by the usual methods. Although the corresponding fractions of the two series of oils have similar molecular weights, the "B" oils were considerably more viscous as shown in the following table of results :—

Viscosities of Fractions from Experiments 45–50.

Fraction.	Viscosities in centipoises at :— 20·0° C.	50·0°	80·0°
5A ..	39·9 ..	9·37 ..	3·80
6A ..	110 ..	18·9	6·54
7A ..	382 ..	40·8 ..	10·8
5B ..	78·1 ..	14·0 ..	4·90
6B ..	333 ..	34·8 ..	9·02
7B ..	455 (at 30°) ..	85·8 ..	17·0

Note.—$T(\text{Redwood seconds}) = 192{\cdot}3\ kv. \left(1+\sqrt{1+\frac{0{\cdot}01952}{(kv)^2}}\right)$

where $kv = \text{kinematic viscosity} = \frac{\text{viscosity in centipoises.}}{\text{density} \times 100}$

Thus 39·9 centipoises above corresponds to 192 seconds (Redwood).
and 455 „ „ „ 2038 „ „

The distillates of the "A" series varied from colourless to yellow, those of the "B" series were considerably darker in colour. The residue boiling above 250°/10 mm. was in each case a very viscous brown oil, but no separation of solid material occurred in any of the fractions even when they were cooled to –20°.

From the above results and those contained in the previous table, the following general statements may be made regarding the characteristics of the two classes of oils "free" (A) and "combined" (B), formed by the action of aluminium chloride on ethylene under pressure and at ordinary temperature :—

(1) The molecular weights of the two types of oils *in the same boiling range* are similar if not identical.

(2) The "A" series of hydrocarbons are mainly of C_nH_{2n} type, together with some C_nH_{2n+2} hydrocarbons, which occur to the greatest extent in the lower-boiling fractions ; on the other hand, the "B" series of oils contain less hydrogen than is required by the formula C_nH_{2n}, and would seem to consist of C_nH_{2n} hydrocarbons admixed with hydrocarbons of lesser hydrogen content such as C_nH_{2n-2}, etc.

(3) The distillates of the "A" series have a lower refractive index, lower viscosity, and lower specific gravity than corresponding distillates (of similar molecular weight) of the "B" series, revealing their different chemical constitutions.

(4) The bromine values (Francis method) of the "B" series of oils, though somewhat variable, were on the average much higher than those of the "A" series. Thus the "B" oils had bromine numbers of about 30–40, while the "A" oils had values averaging about 5.

In agreement with these figures, it was found that the iodine values (Wijs) of the "B" oils were high and those of the "A" oils low. Thus fraction 5A gave a Wijs number, after 30 mins. contact, of 6·9, while fraction 5B, under similar conditions, gave a value of 64.

(5) Finally, it was observed that the "B" distillates possessed the property of combining directly, in the cold, with powdered aluminium chloride to form pasty viscous double compounds, whereas the "A" oils did not exhibit this behaviour.

These results led to the belief that, whereas the "A" oils consisted mainly of saturated hydrocarbons (cycloparaffins with some paraffins in the lower fractions), the "B" oils consisted partly of unsaturated hydrocarbons, probably olefines. Unfortunately it has not been possible to settle the matter beyond dispute, but the following facts throw further light on the question and support the contention that unsaturated hydrocarbons are present in the "B" series of oils :—

(*a*) The distillates of the "B" series, including the lower fractions, are acted upon readily by cold 87 per cent. sulphuric acid, considerable solution taking place and some darkening and tar formation. The "A" oils are stable towards 87 per cent. sulphuric acid in the cold.

(*b*) Attempts to prepare double compounds between "B" oil fractions and methanol solutions of mercuric acetate did not yield crystalline double compounds (characteristic of some olefine hydrocarbons), but reduction of the mercuric salt took place with the production of a mercurous salt.

(*c*) On shaking the "B" oils with cold alkaline permanganate for several hours, oxidation took place and quantities of higher fatty acids were formed, but no ketones could be identified. Lower fatty acids were also formed as evinced by the disagreeable odour of the product, reminiscent of butyric acid and its immediate homologues.

Oxidisability of Oils from Experiments 45–50.—The tendency of oils to undergo oxidation at elevated temperature is of great importance in the case of lubricating oils, and accordingly, since fractions 5–7 inclusive possessed the viscosities of commercial lubricants, it was deemed of interest to examine the tendency

to oxidation. Wilson and Allibone's oxidation test[5], in which the oil is heated to 170° for 6 hours, and a slow current of oxygen drawn through, was used. Undoubtedly a good criterion of the action of oxygen is to examine the change of viscosity of the oil due to this treatment. Unfortunately not enough oil was available for this purpose, and accordingly the extent of oxidation was gauged from the change in density of the oil.

Qualitatively, it was noted that the change in density did actually correspond to a change of viscosity. The results of an experiment on fractions 7A and 7B, and also on a blend of two petroleum red lubricating oils of similar viscosity are given below :—

Oxidation Tests.

Oil.	D^{20}_4 Before.	D^{20}_4 After.	Change in D^{20}_4
Expts. 45–50 Fr. 7A ..	0·8332 ..	0·8529 ..	0·0197
Ditto Fr. 7B	0·8636 ..	0·8933 ..	0·0297
Petroleum lubricating oil..	0·9216 ..	0·9241 ..	0·0025

It will be noted that the change in density was very much greater in the case of the synthetic oil.

Polymerisation of Ethylene under Pressure in the Presence of Aluminium Chloride at Higher Temperatures.

The employment of higher temperatures in the action of aluminium chloride on ethylene under pressure resulted in the following changes in the course of the reaction and type of products :

(1) With increasing temperature the condensation of the ethylene took place with increasing rapidity, on the other hand the life of the catalyst became shorter probably due to the formation of carbonaceous material.

(2) At temperatures up to about 100°, both free and combined oils ("A") and ("B") series, were obtained, but at higher temperatures only traces of oil could be obtained from the highly carbonaceous aluminium chloride double compound. With increasing temperature the "B" oils tend to become more and more unstable and darker in colour.

(3) Rising temperature tends to produce free oil of increasing volatility and containing more and more low-boiling constituents. Simultaneously gaseous paraffin hydrocarbons begin to appear in the residual gas, but no higher olefines and little hydrogen.

In the following four experiments (Experiments 28-31) 30 gm. of aluminium chloride and 50 gm. of aromatic-free petroleum ether were heated with ethylene in the 2 litres autoclave at 75°, 100°, 150° and 180° respectively. At the latter temperature the reaction

was extremely rapid and the products of considerable volatility. The average pressure throughout these experiments was about 35 atm. In Experiments 30 and 31 no "B" oils were obtained, the aluminium chloride double compound having been converted into a highly carbonaceous residue. The data relating to these experiments are tabulated below. (The oil yields do not include the original 50 gm. of petroleum ether.)

Experiments 28–31.

Expt.	Temp. °C.	Duration hours.	Atm. of C_2H_4 absorbed.	Rate of pressure reduction atm./hr.	Oil yield in gm. Free oil.	Combined oil.
28	75	16	47	3·0	83	32
29	100	16	68	4·3	124	27
30	150	18	212	12·0	180	—
31	180	6	130	21·7	140	—

It will be observed that the yield from Experiment 31 is smaller on account of the smaller time of reaction, but the rate of pressure reduction is the greatest with the highest temperature used.

The free oils obtained in the above experiments were yellow fluorescent liquids of increasing volatility as the temperature of the experiment increased. The presence of the diluent (petroleum ether) rather obscures this point however. The analyses of the residual gas are of interest in showing the cracking effect of the aluminium chloride. Practically no paraffins were present in the gas from Experiment 28 due to the lower temperature used. The residual gas from the Experiment 29 had a volume of 35 litres and contained H_2 1·2 per cent., and C_nH_{2n+2} 5·8 per cent. ($n=2·50$). From Experiment 30, 49 litres of residual gas containing H_2 1·8 per cent. and C_nH_{2n+2} 9·2 per cent. ($n = 2·46$) were obtained, and from Experiment 31, 37·5 litres containing H_2 1·8 per cent., and C_nH_{2n+2} 17·6 per cent. ($n = 3·15$). (The hydrogen present in these gases is probably derived from the small amounts of hydrogen present in the original ethylene.)

Experiment 33. *Aluminium Chloride without Diluent at* 100°.—The experiment was designed to test the way in which the activity of the aluminium chloride catalyst decreases with time and also to obtain synthetic oils free from contamination with diluting liquids. 30 gm. of finely powdered aluminium chloride were introduced into the 2 litre autoclave, the temperature of which was maintained at 100°. The ethylene pressures averaged 35–40 atm., the maximum pressure being 55 atm. The experiment was run for three periods of about 30 hours each with continuous rotation. At the end of each period, the autoclave was cooled and the free oil removed (taking care to leave the carbonaceous aluminium chloride complex in the autoclave) and weighed. The autoclave

was then sealed, ethylene introduced, and the autoclave again heated to 100° for a further period of approximately 30 hours. At the end of the experiment the weight of the carbonaceous insoluble residue was found to be 190 gm. In the following summary of the results the weights of oil obtained are high owing to the presence of some dissolved ethylene.

Experiment 33.

	Hours.	Atm. of C_2H_4 absorbed.	Pressure reduction atm./hr.	Wt. of crude oil in gm.
First period	30	120	4·0	202
Second period	31	67	2·2	117
Third period	29	42	1·4	84
Total	90	229		403

The free oil obtained was clear and of a pale yellow colour, having a marked fluorescence. It was distilled up to 100° under normal pressure and afterwards under a pressure of 10 mm. The distillates were colourless or pale yellow.

Distillation of Oil from Experiment 33.

Fr.	Boiling range. °C.	Wt. of fraction gm.	Per cent.	Density of fraction D^{20}_4
1	31°–100°/750 mm.	40·5	12·2	0·6577
2	100°/750 mm.–100°/10 mm.	89·5	27·1	0·7370
3	100°–150°/10 mm.	64·2	19·4	0·8009
4	150°–200°/10 mm.	48·5	14·7	0·8462
5	200°–250°/10 mm.	40·2	12·1	0·8671
6	Above 250°/10 mm.	48·0	14·5	—

Experiment at 150°.—Several experiments on the action of aluminium chloride at 150° (with and without a liquid diluent) were carried out and about 1300 gm. of synthetic oil was obtained.

In a typical experiment using 30 gm. of powdered aluminium chloride, without addition of a liquid diluent, at 150° in the 2 litre autoclave (maximum pressure of ethylene, 55 atm.), a pressure reduction of 128 atm. took place in 6 hours corresponding to a rate of 21·3 atm. per hour. On opening the autoclave, 210 gm. of crude oil were obtained together with 78 gm. of carbonaceous residue, of which 30 gm. were aluminium chloride. The synthetic oil had the following distillation characteristics :—

Boiling range.	Per cent. by weight.
Fraction boiling up to 100°/750 mm.	27·9
100°/750 mm.–100°/10 mm.	33·2
100°–150°/10 mm.	7·3
150°–200°/10 mm.	13·0
200°–250°/10 mm.	10·6
Above 250°/10 mm.	8·1

Experiment 32*b* was carried out in the 2 litre autoclave at 150° to determine the rate of decline of catalytic activity of the aluminium

chloride. 50 gm. of powdered aluminium chloride were used and the experiment was carried out discontinuously for four days, the oil formed after each day being removed before proceeding. At the end of the four days, 143 gm. of carbonaceous matter, consisting of the 50 gm. of aluminium chloride and 93 gm. of complex organic material, were obtained together with free oil. The yields of oil and pressure reduction data given in the following table show clearly the rapid decline in the activity of the aluminium chloride catalyst.

Experiment 32B.

Days.	Hours each day.	Atm. of C_2H_4 absorbed.	Pressure reduction rate. atm./hr.	Free oil gm. each day.	Distillation of total free oil formed. Boiling range.	% by weight.
					28°–100°/750 mm. ..	29·4
1	7·5	154	20·5	232	100°/750 mm.–100°/10 mm.	30·2
2	9·5	125	13·1	196	100°–150°/10 mm. ..	4·0
3	5·5	60	10·8	109	150°–250°/10 mm. ..	15·2
4	5·5	42	7·6	109	200°–250°/10 mm. ..	9·2

Other experiments in which a liquid diluent (petroleum ether, or crude synthetic oil from previous experiments) was used, with the same amount of aluminium chloride at 150°, gave a similar rate of pressure reduction of ethylene, namely, 20 atm. of ethylene per hour initially. Saturation of the liquid diluent with dry hydrogen chloride did not increase the rate of ethylene condensation.

EXAMINATION OF OILS FROM EXPERIMENT 32, PRODUCED AT 150°.

More than a kilogram of synthetic oil produced by the action of aluminium chloride on ethylene at 150° was carefully distilled after first being washed with alkali to remove traces of hydrochloric acid and dried. The following table gives the distillation data of the oil.

Distillation of Oil from Experiment 32.

Fraction.	Boiling range.	Wt. of Fraction. gm.	Per cent. by weight.*
..	I.B.P. = 27°/743 mm.	— ..	—
1 ..	27°–50°/743 mm.	95·0 ..	7·6
2 ..	50°–100°/743 mm.	182·0 ..	14·5
3 ..	100°–150°/743 mm.	189·5 ..	15·1
4 ..	150°–200°/743 mm.	160·0 ..	12·8
5 ..	200°/743 mm.–100°/10 mm. ..	37·5 ..	3·0
6 ..	100°–120°/10 mm.	53·0 ..	4·2
7 ..	120°–140°/10 mm.	47·5	3·8
8 ..	140°–160°/10 mm.	82·0 ..	6·6
9 ..	160°–180°/10 mm.	93·0 ..	7·4
10 ..	180°–200°/10 mm.	65·0 ..	5·2
11 ..	200°–220°/10 mm.	49·5 ..	4·0
12 ..	220°–250°/10 mm.	88·0 ..	7·0
13 ..	Above 250°/10 mm.	110·0 ..	8·8
		1252 gm. ..	100·0%

* of total distillate.

The above distillates were examined carefully by physical and chemical methods and the results obtained are collected in the following table.

Properties of Oils from Experiment 32.

Fraction.	D^{20}_4	N^{20}_D	Mol. wt.	Elementary analyses. % C.	% H.	Approx. formulæ.
1	0·6297	1·3649	77			
2	0·6625	1·3791	90			
3	0·7078	1·4018	116			
4	0·7460	1·4198	145			
5	0·7761	1·4340	174			
6	0·8017	1·4472	190			
7	0·8319	1·4630	212			
8	0·8604	1·4801	226			
9	0·8902	1·4969	254	87·06	12·84	$C_{18}H_{32}$
10	0·9040	1·5043	275	87·20	12·52	$C_{20}H_{34}$
11	0·9181	1·5143	293	87·66	12·31	$C_{21}H_{36}$
12	—	1·5296	350	87·62	12·01	$C_{25}H_{42}$
13	—	—	428	—	—	—

The first four fractions, boiling up to 200° at normal pressure, appeared to consist entirely of paraffin hydrocarbons for the following reasons. Examination of these fractions by the McIlhiney bromine method showed that unsaturated hydrocarbons were absent since the *addition* bromine numbers were nil in every case. Moreover, aromatic hydrocarbons were absent, consequently these fractions could only consist of paraffins or cycloparaffins. A determination of the critical solution temperatures of these fractions in pure dry aniline showed conclusively that they consisted almost entirely of paraffins. Thus the critical solution temperatures (C.S.T.) and aniline points (temperature of complete miscibility of equal volumes of aniline and hydrocarbon mixture) of fractions 2, 3 and 4 were :—

Fraction.		C.S.T.		Aniline point.
2	..	71·3°	..	70·7°
3	..	72·7°	..	72·7°
4	..	75·9°	..	75·8°

No elementary analyses were carried out on the lower volatile fractions owing to the difficulty of combusting such liquids ; nevertheless, the evidence is conclusive that the main bulk of the lower fractions consists of paraffin hydrocarbons.

Analysis of the higher boiling fractions showed the presence of hydrocarbons of lower hydrogen content. Thus Fraction 9 appears to consist of hydrocarbons having the approximate general formula C_nH_{2n-4}, Fraction 10 of C_nH_{2n-6} hydrocarbons, while Fraction 12 has the formula C_nH_{2n-10}. Of the constitution of these substances no decided opinion can at present be hazarded. The bromine values determined by the Francis method vary considerably with

slight changes in the conditions, but do not normally exceed 10 gm. of bromine per 100 gm. of oil. It is indeed doubtful whether this value actually represents *addition* bromine, since these higher fractions appear to be substituted by bromine with very great ease. Under these conditions it is impossible to state definitely whether unsaturated hydrocarbons are present or not, but the evidence goes to show that the oils are for the most part saturated and assuredly of polynuclear cycloparaffinic (naphthenic) structure. It is possible that addition of bromine to these hydrocarbons takes place not by saturation of a double bond but by the splitting of a bond between two naphthene nuclei.

The densities of these higher boiling fractions from Expt. 32 are considerably higher than the densities of oils of similar molecular weight obtained by polymerisation of ethylene in the cold, and more nearly correspond to the densities of similar petroleum fractions.

A very important fact which points definitely to a polynuclear structure for these higher boiling fractions is the very high viscosities of these oils compared with oils of similar molecular weight prepared (see Expt. 45–50) from aluminium chloride and ethylene at ordinary temperature. The viscosities of Fractions 9, 10 and 11 (Expt. 32) are tabulated below :—

Viscosities of Oils from Experiment 32.

Fraction.	Mol. wt.	Viscosity in centipoises at :— 20°	50°	80°
9	254	47·7	9·77	3·66
10	275	192·	23·1	6·75
11	293	375·*	66·7	13·6

* (At 30°.)

Thus it will be seen that Fraction 9 (Expt. 32), with a molecular weight of 254 has a considerably higher viscosity at 20° (47·7 centipoises) than has Fraction 5A (Expt. 45–50), with a molecular weight of 309 and a viscosity of 39·9 centipoises at 20°.

The variation of the viscosities of Fractions 9, 10 and 11 (Expt. 32), with temperature over the range 20°–80° can be represented with a fair degree of accuracy, by an expression of the type of Slotte's formula, namely :—

$$\log_{10} n^t = K^1 - x \log_{10} (A+t) \quad \text{or} \quad n^t = \frac{K}{(A+t)^x}$$

where n^t = viscosity at temperature t°
t = temperature in °C.
and K, K^1, x and A are constants.

The viscosities of these oils fall off more rapidly with rise in temperature than is the case with commercial lubricating oils of similar viscosity.

Oxidisability of Heavier Fractions from Expt. 32.—As an indication of the extent to which oxidation proceeded at 170° for 6 hours in a stream of oxygen, the change of density was noted, as well as the change of density of commercial oils of similar viscosities under the same conditions. The results were as shown in the following table :—

Oxidation of Oils from Experiment 32.

Treated with O_2 at 170° for six hours.

Oil.	D^{20}_4		Change in D^{20}_4
	Before.	After.	
Fr. 9—Expt. 32	0·8902	0·9117	0·0215
Petroleum spindle oil	0·8882	0·8894	0·0012
Fr. 10—Expt. 32	0·9040	0·9302	0·0262
Petroleum oil blend	0·8972	0·8984	0·0012
Fr. 11—Expt. 32	0·9181	0·9404	0·0223
Petroleum blended red oil	0·9216	0·9241	0·0025

It will be noted that the density changes in the case of the synthetic oils are ten to twenty times as great as those registered by the commercial oils. In agreement with this it was noticed qualitatively that the viscosities of the synthetic oils were greatly increased by the oxidation process.

Value of High Boiling Synthetic Oils as Lubricants.—A good lubricant is a substance possessing, to some degree, all of the following properties :—

(1) The property of forming stable films on the surfaces of metals even under pressure.

(2) Sufficient viscosity and comparatively flat temperature-viscosity curve.

(3) Resistance to oxidation at elevated temperatures.

The higher boiling fractions of oils produced by the action of aluminium chloride on ethylene under pressure are pure hydrocarbon mixtures, almost colourless, and having viscosities similar to those of petroleum lubricating oils. Furthermore, the synthetic distillates contain no paraffin wax, for when they are cooled to a low temperature no separation of solid material takes place. It remains to be seen whether these oils fulfil, in other respects, the requirements which would be met by a good lubricant.

As regards viscosity-temperature curve, the oils obtained at high temperature fall off in viscosity much more rapidly than the oils produced at low temperatures ; nevertheless commercial lubricants have, in general, flatter temperature-viscosity curves than either of these two classes of oils. These facts are shown by the curves in Figs. 1, 2 and 3, where the variations of viscosities of synthetic oils and various petroleum lubricating oils with temperature are shown.

Experiments on the change of densities of synthetic and commercial oils, when treated with oxygen according to the method

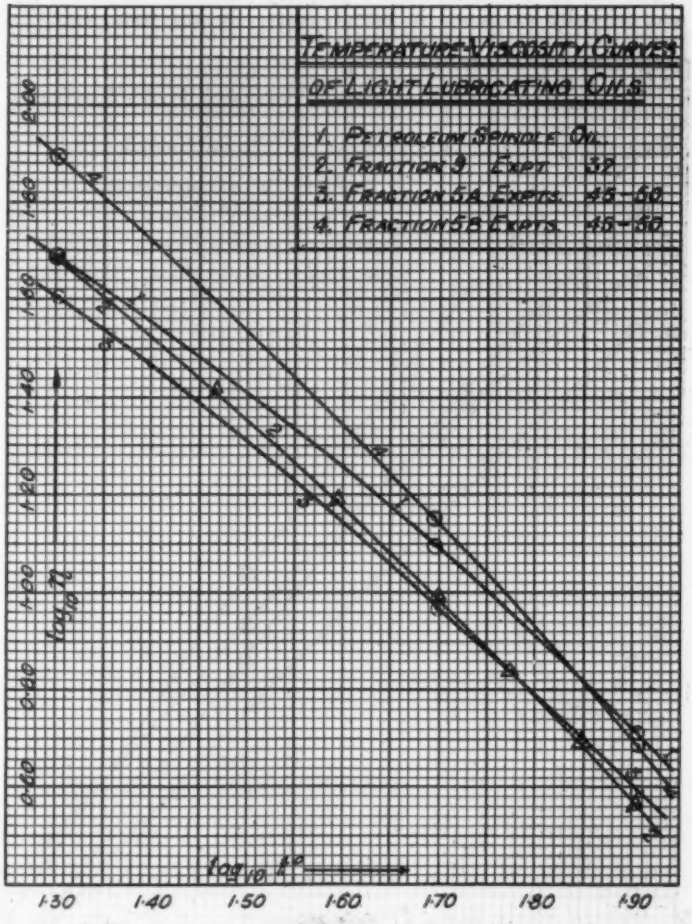

Fig. 1.

of Wilson and Allibone, show that the synthetic oils are much less resistant to oxidation than commercial petroleum lubricants.

Mechanical Tests of the Synthetic Lubricants and General Remarks on the Oiliness Property.

The oiliness of a lubricant is a property which has been carefully and critically examined in recent years. In the past, viscosity

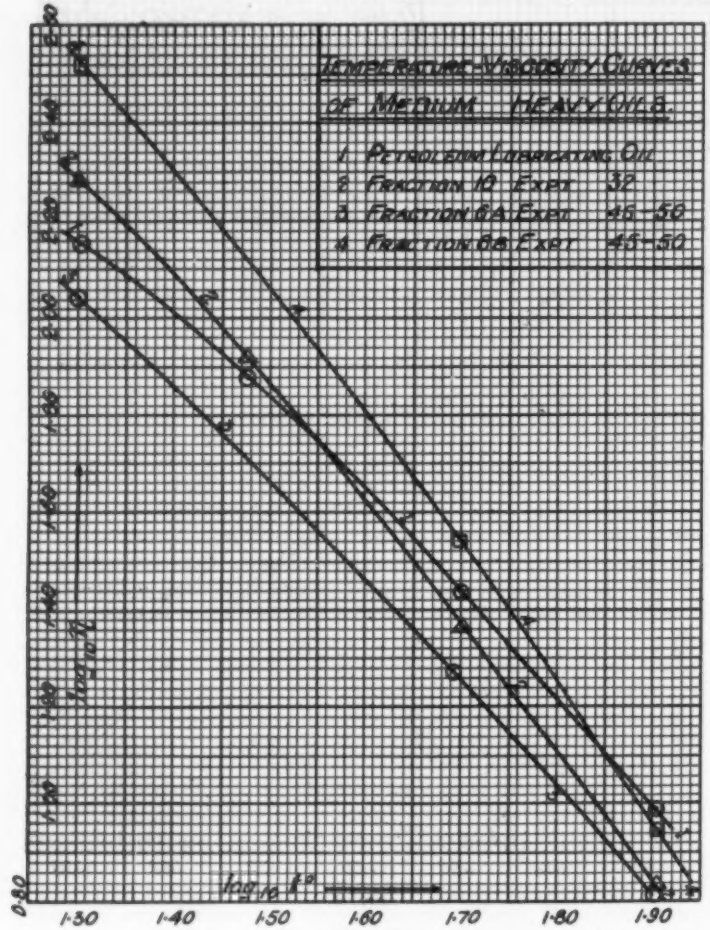

Fig. 2

alone was the criterion of the value of a lubricant; however, as the conception of oiliness, or friction reducing power, developed,

much research was devoted to this problem. The latter research took two different trends, namely, the accurate measurement of friction between surfaces lubricated with pure substances such as

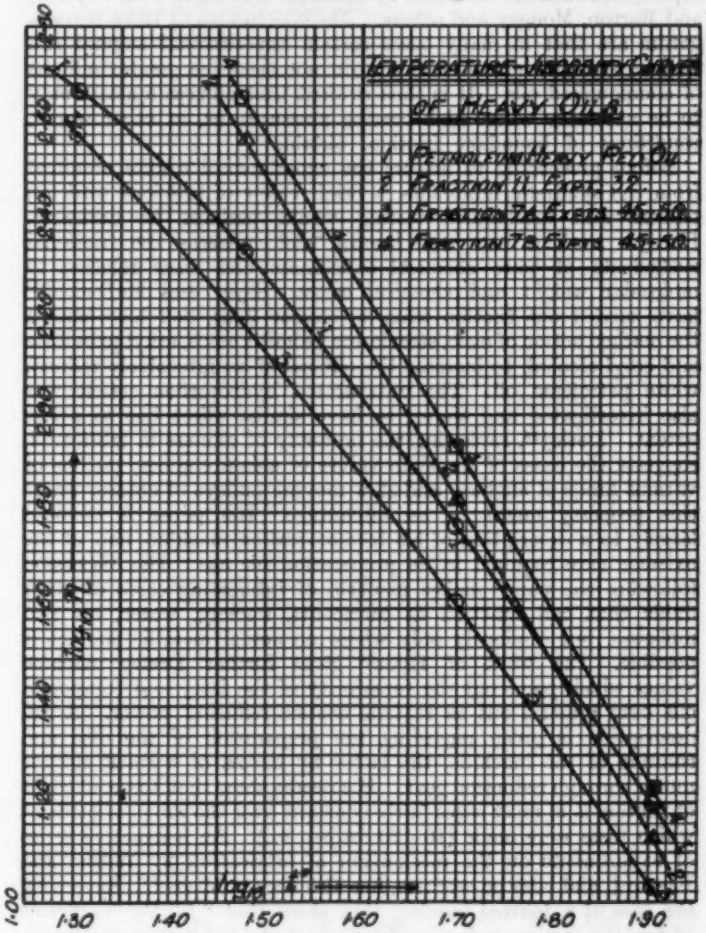

FIG. 3.

the work of Hardy[6] and his collaborators, and the development and application of friction testing machines under conditions where oiliness was a powerful factor, such as the work of Deeley[7], Hyde[8],

Wilson and Barnard[9], Stanton[10], Herschel[11], and others. Of late, researches on lubricants have involved an even more practical aspect, and such are described by Marshall and Barton, Thornycroft and Barton, Mougey and others. The conclusions of these investigators are that in many cases certain experimental engines run well on straight mineral oils and do not need the greater oiliness of compounded oils. It is then evident that oiliness appears only to be necessary where high-bearing pressures, or, in other words, conditions of boundary friction, obtain.

Before proceeding to discuss the experimental results obtained from the synthetic lubricants, a brief review of previous work on oiliness and mechanical testing would perhaps be desirable. Hardy's work is now well known, and concerns the frictional coefficients of pure chemical substances and their relation to molecular weight and chemical series. Seyer and McDougall[12] have carried out friction tests on similar lines, and have shown the marked action of oleic, stearic and palmitic acids, ethyl palmitate and cetyl alcohol, to increase the oiliness of an intensively refined, white petroleum oil. The unsaturated hydrocarbon cetene was also investigated and shown to have similar effect but to a less extent. Deeley[13], reviewing the necessity of oiliness in lubricants, suggests the cases of the slide valves of steam engines, pistons of various kinds of engines, and slow moving pulleys of cranes, where this property might be an advantage. His paper is devoted largely to a description of his friction-testing machine, and of the extreme care required in its preparation for use. The discussion following the paper makes mention of interesting cases of other fluids that can function as lubricants, namely, water, air and molasses, but obviously only where no actual metallic contact is possible. The work of Hyde[14] gives further Deeley machine values which point out the superiority of the fatty and compound oils over mineral oils as regards friction-reducing power. A full description is given regarding the preparation of the disc and running of the machine, the latter by means of a small electric motor through reduction gear. His results show that the coefficient of friction is in most cases fairly constant over the range of loads at which tests were made (10–120 lbs./sq. in.). An instructive series of experiments on the mechanism of lubrication by Wilson and Barnard, and later co-workers, has also been published. Reviewing the case of a journal bearing, they show that "f" the coefficient of friction is some unknown function of at least nine variables :—

z, n, p, c, d, l, S, M, and O, where
z = viscosity of the lubricant at the operating temperature ;
n = revolutions per minute ;
p = pressure on bearing ;
c = diametrical clearance of bearing ;

d = diameter of journal;
l = length of bearing;
S = surface conditions (kind of metal, smoothness, etc.);
M = method (and amount) of oiling;
O = oiliness factor of the lubricant.

Thus is deduced :—

$$f = \phi\left(\frac{zn}{p}\frac{c}{d}\frac{l}{d}S, M, O.\right)$$

The characteristic shape of the curve obtained by plotting zn/p against the coefficient of friction is now well known. The curve can be divided into three sections corresponding to perfect film lubrication, critical point and region of partial (boundary) lubrication. An interesting deduction is made from their conclusions, namely, that the average oil-testing machine operating in the region of fluid film lubrication is nothing but a very crude type of viscometer, giving no information as to the oiliness of the lubricant. In experiments on oiliness these investigators employed five methods to obtain information, namely: (1) the use of a Deeley type machine; (2) a refined and reproducible method of determining static friction between partially lubricated surfaces; (3) the measurement of the interfacial energy between oil and mercury; (4) the measurement of the electrical resistance and the rate of formation of adsorbed films on metal surfaces, and (5) the clogging of the fine metal capillaries through which lubricants are forced. They found that, in the light of the results obtained by the above-mentioned methods, the static friction test with proper refinements was probably the best single measure of the properties of oiliness, but it should be supplemented by measurement of the thickness of the adsorbed film at high pressure in order to throw more light on the mechanism of the action of different constituents in lubricating oils. Their apparatus for static friction involving the inclined plane is worthy of notice. In passing, some interesting experiments were made in which it was shown that a preparation of active iron could remove to some extent stearic acid from a non-polar oil medium.

The experiments of Dover, in which the lubricating efficiencies of oils were determined on a Deeley machine, present results which differ from those of Hyde; however, the metals used were not the same. Dover[15] tested various oils at 22° C. and 6 r.p.m., and found considerable lowering of the static coefficient of friction with increasing load (from 10 to 100 lb. per sq. in.). With the view of employing higher pressures when testing oiliness of lubricants in order to avoid the possible variation in the coefficient of static friction with load, Herschel[16] has evolved an oiliness machine, which resembles the Deeley machine in some respects. The disc is

motor driven at very low speeds and it is possible to obtain the coefficient of friction of rest and of slow motion. The slip takes place between the rotating disc and a slider supported on three ¼-in. steel balls of the type used in ball bearings. The disc, which may be of any metal, is similar to that used in the Amsler Wear Test Machine[17], and the slider is similar to the type used by Koethen[18]. The slider is not weighted, since a very high pressure is possible with the point contact. This machine appears to be little known in this country, but will, without doubt, prove of great value in oiliness evaluations. Another oiliness machine of the inclined plane type has also been described recently[19]. The effect of ozone treatment on the oiliness of oils has been investigated by Dover and Appleby[20], and a decrease was noted after such treatment in the case of a vegetable oil and an increase with mineral oils.

Reviews of work on oiliness and lubrication and descriptions of testing apparatus are given by Lincoln[21], Wilharm[22], Woog[23], Ascher[24], Ries[25], Parsons and Taylor[26], Gill and Gill[27], Gilson[28], Hersey[29], Karplus[30], Kingsbury[31], McKee[32], and Marvin[33].

Experimental.

The synthetic lubricating oils from ethylene were tested as regards durability on a Thurston machine and for oiliness by means of a Deeley machine.

Durability.—For the reasons stated by Wilson and Barnard[34] and Nash and Bowen[35], it is unwise to use the rotating shaft-bearing type of machine for oiliness determination, but it has been found possible to obtain from this type of instrument relative values for the durability of two oils when extreme care is taken to carry out runs under identical conditions. The durability factor of any oil is the time a certain quantity of the oil functions as a satisfactory lubricant under the selected conditions, and will depend on many physical and chemical properties of the oil in question. A definite amount of oil was added to the bearing (2 to 3 drops), and the machine run at certain selected loads and speeds according to the nature of the oil, and observations were taken as regards heat of bearing and duration of steady value of the friction reading. Comparative tests were conducted with commercial oils of similar viscosity, all conditions being adjusted to be identical.

The results recorded are the averages of many such runs.

It was found that whereas the synthetic oil produced at high temperatures (Experiment 32), and also the low temperature oils of the "A" series (Experiments 45–50) showed much lower durability

figures than the corresponding petroleum oils, yet the comparatively unsaturated "B" series oils showed durability values practically as good as those of the petroleum lubricants; a result quite unexpected.

Oiliness.—The experiments described here were carried out on a Simplex Model of the Deeley Machine. The machine was hand driven and to obtain consistent results with the less oily lubricants, a very slow speed of 1 r.p.m. was found to be desirable. The surfaces were prepared, as previously described, by grinding in with carborundum powder and it was found safer to wash the surface with warm water rather than ether or petroleum ether after fatty or compound oils had been under test.

Deeley Friction Tests on Various Oils.

Type of oil.	Load/sq. in.	Deeley value of coefficient of friction, cast iron—cast iron.
Fatty :—		
Sperm oil	50 lb. ..	0·126
	100 lb. ..	0·121
Vegetable :—		
Rape oil	50 lb. ..	0·111
	100 lb. ..	0·111
Blown rape oil..	50 lb. ..	0·136
	100 lb. ..	0·131
Mineral :—		
Spindle oil (1)	50 lb. ..	0·170
	100 lb. ..	0·165
White spindle oil	50 lb. ..	0·194
	150 lb. ..	0·194
B.P. medicinal paraffin oil	50 lb. ..	0·216
	100 lb. ..	0·213
"Germ Processed" oils :—		
White spindle oil + 1% oleic acid ..	50 lb. ..	0·109
	100 lb. ..	0·107
B.P. medicinal paraffin + 1% oleic acid	50 lb. ..	0·107
	100 lb. ..	0·105
Oxidised oil :—		
B.P. medicinal paraffin oil blown with	50 lb. ..	0·158
oxygen at 170° C. for four hours ..	100 lb. ..	0·162

Deeley Friction Test on Synthetic Oil from Ethylene.

Oil.	Boiling range.	Load/sq. in.	Deeley value of coefficient of friction.
Expt. 32 Fr. 9 ..	160°–180°/10 mm. ..	50 lb. ..	0·182
		100 lb. ..	0·167
Expt. 32 Fr. 10 ..	180°–200°/10 mm. ..	50 lb. ..	0·184
		100 lb. ..	0·170
Expt. 45–50 Fr. 5B ..	175°–200°/10 mm. ..	50 lb. ..	0·180
		100 lb. ..	0·180
Expt. 45–50 Fr. 6B ..	200°–225°/10 mm. ..	50 lb. ..	0·177
		100 lb. ..	0·170
Expt. 45–50 Fr. 6A ..	200°–225°/10 mm. ..	50 lb. ..	0·172
		100 lb. ..	0·170

It will be observed from the above results that the synthetic oils have friction values comparable with those of well-refined straight mineral oils.

If greater oiliness were required such oils could be compounded with fatty oils or "germ processed" with a few per cents. of a soluble fatty acid as described some years ago by Wells and Southcombe in the case of petroleum oils.

As regards the action of fatty acids in lowering the friction coefficient, a series of experiments was carried out with the B.P. medicinal paraffin oil and small quantities of oleic, erucic, palmitic, margaric, stearic and eicosanic acids were found to have similar action; the saturated acids however could only be used in very small concentration owing to their relative insolubility. Oleic acid is quoted in a patent as an example of an acid to be used in "germ processing" synthetic lubricating oils, such as those from destructive hydrogenation of carbonaceous substances by Wells and Southcombe.[36]

Conclusion.

From the results of these experiments, the synthetic oils from ethylene produced in the manner described cannot be classified as equal to petroleum lubricants as regards the tendency to oxidation and as regards durability except in the one case. The former property is of great importance as already the fatty oils have become unpopular on account of their greater tendency to oxidise to gummy bodies than petroleum lubricants. In this connection, the possibility of adding inhibitors such as lead tetraethyl to lower the oxidation tendency should not be overlooked c.f. the patent of Callendar, King and Mardles,[37] and paper of Hatta.[79]

Other substances are also claimed as inhibitors to lubricating oil oxidation such as: approximately 1 per cent. of urea[69] nitrobenzene, and also free sulphur,[76] but the question as to whether these doped oils stand up better to practical conditions of use has recently been raised by Lederer and Zublin.[77]

It is considered by the Authors that inhibitors are only palliatives to this problem and that further research may yield synthetic oil as valuable as petroleum fractions. Refining as it is known with petroleum distillates will be practically unnecessary with these synthetic oils and will mainly depend on the purity of the original ethylene gas. As wax is absent this refining is still further simplified. Stability, concerning both chemical reactions, oxidation, and polymerisation, is the most desirable feature in lubricating oils. Uniformity in physical properties such as maintenance of viscosity with temperature is also desirable. It will have been

observed that while some of the synthetic oils had steeper temperature-viscosity curves than corresponding petroleum lubricating oils, others had curves more similar. Further research will be directed towards the production of synthetic oils of even greater stability and uniformity.

As regards oiliness this property of a lubricant has not the significance which was ascribed to it until recently. For several purposes, practical tests have shown that the oiliness of a straight mineral oil is sufficient as pointed out by Marshall and Barton[38], Thornycroft and Barton[39], and Mougey[40]. However, in some cases where high-bearing pressures obtain, the oiliness factor is of more importance. Most bearings go through a condition of ruptured film lubrication when starting and stopping, and Wilharm[41] points out that in some electrical machinery the bearing pressures have become so high that it is doubtful whether a fluid film forms at all. This investigator mentions also gears, pistons and cross heads as possible cases for an oily lubricant, and also quotes the insurance factor against damage in the event of discontinued oil supply due to mechanical defect.

Oiliness is thus of less importance than stability, owing to the ease with which this former property can be obtained by judicious compounding with fatty oils or fatty acids. With the usual refining, petroleum lubricants appear to possess all the oiliness required for many practical applications.

Before dismissing the subject of lubrication reference should be made to the modern tendency to develop special lubricants for each practical application, a tendency which may affect future lines of research on synthetic oils. One type of lubricant containing zinc oxide is designed for a certain type of gear and electroplating action is claimed[42]. Numerous lubricants have been patented which contain metallic soaps, and an American example is claimed to contain lead oleates[43]. In this connection a closer study of the friction reducing properties and oil solubility of the lesser known soaps should be made. A study on these lines has been started already[44]. Below is appended a list of references which give information on the compounding of petroleum and other lubricants for special purposes and on lubrication problems generally.[45–80]

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DISCUSSION.

Dr. F. B. Thole congratulated Prof. Nash and his colleagues on having carried out a research of notable interest both to chemists and to petroleum technologists since it linked together the simple hydrocarbon ethylene and a complex product which resembled in a number of respects a natural petroleum. Liquid hydrocarbon products had of course been obtained from other simple gases such as methane and acetylene, and in these cases tentative theories had been put forward ascribing to these hydrocarbons the origin of petroleum. It was subsequently shown of course that these synthetic " petroleums " did not bear such a close resemblance to natural oil as their superficial appearance at first suggested.

In the present case the polymerisation products appear to contain a number of hydrocarbon types known to be present in the lower boiling fractions of petroleum, but the special interest of the research was directed to the higher fractions which possess considerable viscosity and lubricating qualities. The heaviest fraction, especially of the B class, bears a striking resemblance to the highest boiling fractions of Badapur crude oil which, though very viscous, are sticky rather than oily and also have very steep viscosity-temperature curves.

He would like to ask if the authors had made any comparison between the viscosities of narrow-cut fractions of corresponding boiling point from their synthetic oil and from petroleum lubricating oils (paraffinoid or naphthenic types). The apparent difference in the samples shown suggested that some comparative data would be interesting and these data are shown in the following table :—

Material.	Boiling Range at 10 mm.	Viscosity in Centipoises at 20° C.	at 50° C.
Synthetic oil 6A	200–225°	110	19
„ 7A	225–250°	382	41
„ 6B	200–225°	333	35
„ 7B	225–250°	455 at 30° C	86
Persian Lub. Oil	195–230	40	10.6
	230–250	56	13

It will be noted that the synthetic oils are all very much more viscous than the fractions of equal boiling point prepared from a natural petroleum. It would be of considerable interest to follow up and elaborate this contrast between corresponding fractions of synthetic and natural oils.

He also asked if the authors had any confirmatory evidence as to the suggested formation of A oils by a splitting-off process from the aluminium chloride—B oil complex. The characteristics of

the B oils seem so markedly different from those of the A oils, that it seemed rather difficult to visualise such an intimate relation between the two as this mode of formation would presume. Did any action occur if A oil was allowed to stand in contact with aluminium chloride—B oil complex in the absence of additional ethylene, and did aluminium chloride react readily with an A oil to give an aluminium chloride—B oil complex ?

Mr. E. C. Craven expressed Dr. W. R. Ormandy's regret that, having been obliged to go abroad at short notice, he was unable to be present to join in the discussion on the work of Professor Nash and his colleagues. He knew that Dr. Ormandy had been looking forward with a very lively interest, indeed, to the publication of those researches, and that interest had been whetted by an early notification in general terms which Professor Nash had been good enough to send to him.

It would be remembered that some few years back Dr. Ormandy and himself had published considerable work showing that olefines, when treated with concentrated sulphuric acid, yielded saturated hydrocarbons and highly unsaturated hydrocarbons. In particular, 3 molecular proportions of an open chain olefine appeared to yield 2 molecular proportions of open chain paraffins and 1 molecular proportion of triolefines, and it was shown by a carbon balance sheet that these bodies were the sole products of the reaction. This production of open chain paraffins was so opposed to all preconceived notions that, with a few praiseworthy exceptions, the chemical world appeared to take considerable umbrage in respect of this discovery. It was, therefore, with the greatest pleasure that he found that the very distinguished authors of the present paper had obtained almost parallel results, albeit with quite another reagent. These results they had, very properly for themselves, interpreted with considerable caution, and he conceived it his duty to amplify their deductions.

He desired, first of all, to put forward the hypothesis that in the work which had been described there was found not one general reaction but two; one being a finite chemical reaction with the aluminium chloride and the other the polymerisation of ethylene in solution. The reaction with aluminium chloride might be parallel to the reaction already described with sulphuric acid, while the polymerisation in solution probably gave rise to cyclic bodies.

Turning to the paper itself, under the polymerisation of ethylene without catalysts, it was stated that the pressure fell uniformly from 140 to 32 atmospheres. If this meant that the pressure fall was a straight line, it was obvious that the reaction velocity

was much greater at the end of the experiment than at the beginning. In other words, the oil formed catalysed the polymerisation. Patents had been taken out covering the polymerisation of ethylene in kerosine. It was obvious also, therefore, that in experiments with aluminium chloride that polymerisation must be proceeding side by side with the chloride reaction proper.

In most of the aluminium chloride experiments there were 3 parts of "free" oil to 1 part of "combined oil." A very similar proportion of free and combined oils was obtained when higher olefines were treated with sulphuric acid. The free oils from experiments 45-50 had been very thoroughly examined by Professor Nash and his colleagues, and they stated that they were mainly cyclic paraffins with some open chain paraffins. He desired to suggest that it would be more accurate to say that they were mainly open chain paraffins with some cyclo-paraffins. Calculations from the hydrogen/carbon ratio and also from the optical properties of the fractions gave results which were in reasonable agreement, and the mean figures were as follows :—

Fraction.	% open chain paraffins.
1A	68
2A	69
3A	76
4A	60
5A	65
6A	43
7A	28

The "B" fractions were distinguished by a low hydrogen content accompanied by a low bromine absorption. He suggested that these fractions contained a proportion of cyclic olefines, which also was indicated by the action of 87 per cent. H_2SO_4 mentioned in the paper.

The oils produced by the action of aluminium chloride at higher temperatures were also of great interest. Calculations of specific refractivity indicated that the first six fractions from Experiment 32 consisted mainly of open chain paraffins, while the heavier fractions were polycyclic in character. It was found by Dr. Ormandy and himself that polycyclic paraffins were formed by the action of sulphuric acid on cyclic olefines or their related alcohols. In the present case it was likely that they were formed by a similar action of aluminium chloride on the cyclic olefines which, as he had already suggested, were present in the combined "B" oils formed at lower temperatures.

It had always appeared to him that the only theory covering the facts of that and many similar reactions was one which he remembered hearing Dr. Dunstan put forward tentatively in relation to

cracking. He supposed that free methylene groups were momentarily formed by fission of ethylene, and that these joined into rings, some of which were stable and some unstable. The breakdown of the unstable rings gave rise to the momentary existence of more complex groups with free bonds, and these combined in various ways. In addition there was direct polymerisation of ethylene to higher olefines, and these suffered fission not necessarily at a double bond. In that way there would be a jumble of alkyl groups and methylene-like groups which would combine according to the chances of collision, giving a wide range of products such as was actually observed.

He dared not take up any more time by venturing on the lubrication side of the present work, and would conclude by thanking the authors for a very interesting piece of work, which must have cost much patience to carry to its present stage. He looked forward to further work by them on the subject of unsaturateds in general.

Mr. E. R. Redgrove congratulated Prof. Nash and his colleagues upon a paper of the deepest scientific interest to all petroleum technologists.

Commenting on the properties of distilled oils from Experiments 45–50, he said that the low density of some of the fractions was surprising and led one to believe that some compounds hitherto unknown in the petroleum world must have been formed. For instance, Fraction 7A had a density of 0·833. Pennsylvanian crude produced some of the lightest density lubricating oils known and a Pennsylvanian lubricating oil of similar viscosity to Fraction 7A would have a density of about 0·875. From records in his possession he would say that the molecular weights of the two were more or less comparable.

The authors stated that they were unable to identify ketones when the " B " fractions were agitated with cold alkaline permanganate, which confirmed his own observations. In all the work he had carried out on the oxidation of lubricating oils, either with permanganate or other agents, he had never been able definitely to identify alcohols, aldehydes or ketones, although such bodies must be formed in order that the fatty acids which were obtained could be produced. It seemed that these lower oxidation products, immediately they are formed, must undergo intermolecular decomposition. This would account for the production of the lower fatty acids which are always found amongst the decomposition products of oxidised lubricating oils.

On the question of the oxidation test applied he was rather surprised to find that the authors had chosen the increase in density of the oil as a measure of the extent of oxidation. Although

increase in density was a measure of increase of viscosity, increase of viscosity might be due to polymerisation, as when certain of the fixed oils were "blown," rather than to decomposition. Some years ago he had carried out an investigation on the chemical stability of certain lubricating oils, using a blowing test similar to that adopted by the Air Ministry, and had found that increase in viscosity was not always a measure of the amount of decomposition. His results showed that at least as far as straight distillate oils were concerned the amount of decomposition, measured by the amount of asphalt formed, was directly proportional to the increase in the coke value, and he would like to know if the authors intended carrying out an investigation of the amount of asphalt formed after the oxidation test, or if they would ascertain the increase in the coke value.

Viewed from the economic standpoint the research was of great importance, not only to the Institution, but to the whole Empire. The Empire, although woefully short of crude petroleum, had abundant supplies of coal and the time might come when the country, for its very existence, would have to lean heavily upon its coal resources. He had always felt that as far as liquid fuel was concerned, coal could be relied upon in an emergency, but the same could not be said about lubricants. The high-speed internal-combustion engines and all the other mechanisms which comprise the engines of peace, and of war, could not be run without lubricants, and although much had been said of wonderful alloys, which by their anti-friction properties, rendered the use of lubricants unnecessary, they were not with us yet. Prof. Nash and his colleagues had earned the thanks of the Institution for the attention they had given to the vital question of lubrication—a subject which was so frequently ignored by investigators in petroleum.

Mr. C. I. Kelly associated himself with the remarks of the previous speakers on the general character of the paper. It was useful in so far as it gave new information, and it also corroborated work which had already been in progress elsewhere for many years. For instance, when Prof. Nash mentioned the fact that ethylene without catalysts polymerised at between 325° and 350° C., he confirmed the statement of Day (1886), that ethylene experienced no change until a temperature of 350° C. was used and then it gave polymerides, having a carbon-hydrogen ratio similar to the olefines.

He certainly agreed with Mr. Redgrove in regard to many of his points. He thought that the authors experienced difficulty in the question of lack of material when they wanted to evaluate the oils as lubricating media. He considered that a far better way

of gauging the progress of the oxidation would have been to carry out the Ramsbottom carbon residue test, for example, after oxidation. It was well known that only 4 grammes of oil were needed for the experiment, and the increase in coke number would serve as a measure of the extent of oxidation; and the results would have been quoted in terms which were becoming more and more readily understood in the trade. It was really very surprising, on the whole, how little use was being made of that very useful and simple test.

The authors had introduced many controversial points. For example they talked about the *addition* bromine, etc., of lubricating fractions. This was a question which caused controversy. As the authors said: "It is doubtful whether the bromine values determined by the Francis method actually represent *addition* bromine." He thought that the general indication at the present time was that heavy petroleum fractions in the main were not unsaturated in the ordinary sense, and that bromine numbers did not represent unsaturation.

The authors went to the extent of oxidising their synthetic oils and comparing them with the oxidation products of petroleum spindle oil, which were referred to as "commercial oils." He thought the grades deserved more definition than merely the name of "commercial oils." He could appreciate the difficulties which the authors had experienced when they wished to express the oxidation tendencies of the oils, but it seemed a little futile to compare them with commercial oils, and to leave it at that, because if the commercial oils were of the Venezuelan or Mexican type it was just possible that the synthetic oils might have shown up better than the petroleum fraction; or if they had taken, for instance, a high-class Pennsylvanian or Peruvian or Russian oil, the differences between the synthetic and the petroleum oils might have been much greater than the figures quoted in the paper. The authors would have given more assistance if they had defined those commercial oils a little more closely, and had let members know a little more about their general characteristics.

He had noticed that most of the contributors to the discussion up to that point had avoided the hackneyed question of oiliness and durability, and possibly if he were to touch on that point a little it might create further discussion. He was inclined to deplore the fact that the authors had ventured to resurrect the hackneyed question of oiliness, especially as an epilogue to a paper on chemical work.

He noticed that the authors referred to "oiliness or friction-reducing power." This was really an indirect method of giving a definition to the term oiliness. It was generally agreed that the

co-efficient of friction was not the measure of the tendency to seizure. If it were, how could it explain the following cases? Lard oil was known to give a better co-efficient of friction than certain transmission lubricants, yet it permitted bearings to seize at about 13,000 lb. per sq. in., whilst the special lubricants resisted seizure up to as high a pressure as 30,000 lb. per sq. in. The work of Mougey on lard oil and transmission lubricants, he thought confirmed the well-known work of Stanton, who showed that certain mineral oils containing non-polar bodies could be found which would provide efficient lubrication at high temperatures long after castor oil failed to provide it. The measurement of the co-efficient of friction of oils to be compared at one temperature under low bearing pressures was inadequate for their relative valuation.

He would, therefore, suggest that although, as the authors mention the synthetic oils have favourable friction values when compared with those of commercial oils, this point really proved very little.

Mr. J. Romney said that the authors, in referring to oiliness, which was a famous debating point, had of course stated that oiliness was only necessary where one had conditions of boundary lubrication, and more or less implied that one did not normally need any oiliness beyond that which was given by ordinary mineral oils. At the same time, would it not be natural to give to ordinary mineral oils a little of that oiliness which fatty oils provided, simply because machinery was not perfect? Temporary mechanical difficulties might occur in machinery and result in breakdown, which a greater amount of oiliness in the oils used might have prevented, if only by the film left from the last time the engine had been running.

With regard to the various mechanical testers, of which the authors seemed to disapprove in general, could any information be given about the recent American device, the "Consistometer," which gave friction readings right up to the temperature where there was a definite breakdown of lubrication indicated by seizure of two metal surfaces? As the price of the machine and accessories was £450, much should be expected of it. The machine was made by the Consistometer Corporation.

Mr. E. J. Dunstan asked whether he was right in assuming that the comparisons of temperature density curves were made between the unrefined synthetic products and the fully refined lubricating oils. Fully refined lubricating oil had had its temperature viscosity curve reduced already to a minimum. If that was

so, it seemed to him hardly fair to compare an unrefined oil with a refined oil. If it was comparing an unrefined oil with an unrefined oil, the temperature viscosity curves might show somewhat of a difference on the graphs.

Mr. W. H. Cadman said he did not know whether Professor Nash had examined the question of low temperature carbonisation, but if so he wished to ask him if he could explain how the synthetic lubricating oils which he had described compared with the lubricating fractions obtained by low-temperature carbonisation of coal.

Mr. S. T. Minchin called attention to a point raised by Dr. Thole about Badapur crude oil. Some investigations had shown quite conclusively that more than 75 per cent. of the "lubricating oil" was soluble in concentrated sulphuric acid, but the paper read before the meeting gave the impression that the "A" series of oils would not be appreciably soluble in this reagent. For this reason he did not think that the products described by Professor Nash and colleagues could be compared with the products from the "lubricating" fractions from Badapur crude.

On the other hand, with regard to the paper read by Professor Nash, it seemed to him that one failure of all attempts to synthesise lubricating oils lay in the fact that nobody knew what the structure of lubricating oils was, even if simply confined to the high grade Pennsylvanian type. The evidence, of course, was fragmentary, but there was a little. Maybury, for instance, and Wilson and Allibone, for another example, said that a portion of the Pennsylvanian type of oils had a series formula of C_nH_{2n-4}, up to molecular weights of about 700. For such series formulæ, it was found impossible for such lubricants to contain more than three polymethylene rings. This part of the molecule would thus have a molecular weight of about 250, leaving a balance of about 450 to be disposed of as side chains. Due to the low gravity of the Pennsylvanian type compared with practically all other petroleum hydrocarbons of similar molecular weight, it appeared that the molecular volume must be considerably greater than practically all other petroleum hydrocarbons of similar molecular weight, and the presumption, at any rate, was that with the Pennsylvanian type of oil the side chains were not so much numerous as long and few.

With regard to the paper just read, in view of the fact that ethylene was known to be an ethylating agent in the presence of aluminium chloride—and it was not definitely known, so far as he knew, whether polymethylenes were ethylated in the presence of ethylene and aluminium chloride—he suggested that the probable

result of ethylene in the presence of aluminium chloride was to tend to form fully ethylated rings. If that was so, it would be seen how greatly the lubricants prepared by such methods might differ from the picture he had given of the Pennsylvanian type. As a possible confirmation of this might be quoted the oxidation results given in the paper. An oil of the fully ethylated type, with a large number of short side chains, would be much more susceptible of oxidation, because it would have many more points of attack for the oxygen; and it was found by the authors of the paper that their oils were more susceptible to oxidation than the commercial grades they tested.

Finally, with regard to the Wilson and Allibone oxidation test, which was mentioned in the paper, it was only fair to the originators of the test to state that they recommended weighing the asphalt formed. He wished to associate himself with other members who would also like to know whether Professor Nash and his colleagues weighed the asphalt formed from their oils.

Mr. G. R. Nixon said that some years ago in some experiments on cracking paraffin wax he had obtained the following results. The petrol fraction of the pressure distillate from the wax approximately consisted of 50 per cent paraffins and 50 per cent. unsaturates. On graded acid treatment of this cracked distillate he had obtained the ordinary polymerised tarry products soluble in the acid, but had also obtained a rather large quantity of polymers soluble in the oil, and the distinctive feature of these polymers was that they were practically colourless. The distillation range of the unrefined petrol was I.B.P. (30° C.)—150° C., whereas that of the acid treated petrol was I.B.P. (70° C.)—400° C. The fraction 150° C.—400° C. appeared to contain cyclic hydrocarbons according to specific gravity, viscosity, refractive index data. A portion of this fraction boiling between 350° and 380° C., approximately, had a viscosity of the order of 70 oil (*i.e.*, 70 seconds Redwood/140° F.). It might be advanced that this viscous fraction was sulphuric acid polymers, but if so they were remarkably stable to heat, giving off no hydrogen sulphide or sulphur dioxide at their distillation temperatures. Also, the refractive index was against them being sulphonated bodies. It appeared to him that a more or less similar effect had taken place in his experiments as had taken place in the aluminium chloride experiments described by the authors—namely, polymerisation of some of the unsaturates by sulphuric acid, the paraffins acting as a diluent. These results are more or less closely allied to Ormandy and Craven's work on the acid treatment of the lower olefines. It certainly showed that the polymerisation of unsaturates to viscous oils could be

accomplished with sulphuric acid as well as with aluminium chloride. He agreed with his colleague, Mr. Minchin, that the synthetic lubricating oils appeared to belong to a different type to that of Pennsylvanian and Hardstoft, but at the same time he thought that the work which Professor Nash had done was a big advance in the synthetic method of preparing lubricating oils.

In conclusion, he would like to ask the authors whether they had investigated the action of selective solvents such as liquid sulphur dioxide on their synthetic products as an aid in determining their constitution.

Professor Nash said, in reply to Dr. Thole, that a comparison of the viscosities of the synthetic oils with petroleum fractions of definite types was very desirable; in fact, he had this aspect of the subject noted down for future research. He hoped that by this synthesis of heavy hydrocarbons, light might ultimately be shed upon the nature of the heavier constituents of natural petroleum. As regards the mechanism of the formation of the two series of oils, the continued accumulation of the A oil and constancy of the amount of B oil per given weight of aluminium chloride was in accordance with the theory put forward in the paper. The chemical characteristics of the A and B oils were explicable on the basis of this isomerisation process. That the first product formed is a higher olefine is readily shown by the fact that, if the time of the reaction is cut short, butylene forms an important product of the reaction.

Mr. Craven's remarks interested him very much indeed, but he could not accept completely his conclusions as regards the mechanism of the ethylene polymerisation. Perhaps the point concerning the polymerisation of ethylene without catalysts had not been clear. This polymerisation was described as being accompanied by a uniform pressure reduction, which was intended to mean a pressure reduction without discontinuity. Actually the pressure fall was not a straight line relationship, being more rapid at the beginning of the experiment—*i.e.*, at the higher pressure. The general confirmation of the results of the olefine-sulphuric acid research of Dr. Ormandy and Mr. Craven was a pleasing issue of the work.

He agreed with Mr. Redgrove that the densities of the synthetic lubricants were lower than Pennsylvanian oils, and he would add that in this respect the oils fell into line with the synthetic lubricating oils produced by the Brownlee process (*i.e.*, polymerisation of liquid olefines in cracked gasoline by aluminium chloride). Mr. Redgrove raised also the question of the oxidation tests of oils. This was indeed a vexed question, and he hoped that members of his research staff would be occupied upon this subject before long. The facts were as follows: the synthetic oils were undoubtedly oxidised

to a greater degree than mineral oils under the same conditions, as evinced not only by the increase in density and viscosity but also by the *amount of water formed*. It is interesting, too, that only very small amounts of asphaltenes were formed in the oxidation of these synthetic oils.

Mr. Kelly had certainly understood the difficulties in dealing with small quantities of oils, especially in the comparative tests with petroleum oils. He must explain that the object of combining physical and chemical tests was to give as completely as possible a description of the oils under review. Mr. Kelly will have gathered from their recent book on lubrication that he and one of his colleagues (A. R. B.) did not consider laboratory friction testing apparatus to give absolute working figures in all cases but comparative figures under the conditions stated. It would be useless, for example, to attempt to correlate Deeley machine figures at 100 lb. per sq. in. with bearing conditions mentioned by Mr. Kelly with pressures up to 30,000 lb. per sq. in. As regards the commercial oils used, these were in all cases high-class products, which would not contain constituent oils from the more easily oxidisable crudes.

As regards Mr. Romney's question, he had no first-hand experience of the "Consistometer," and he ventured to add that its price was rather prohibitive for many laboratories.

In reply to Mr. Dunstan, Professor Nash said that owing to the high purity of the etyhylene, the synthetic oils could be looked upon as refined oils for most purposes. These oils did not contain the asphaltic or cracked products that might be present in a petroleum oil.

Mr. Cadman had raised a question upon which information was very scanty at the present time. Most of the statements in existence were based on laboratory experiments. The latter indicated that the low temperature tar fractions of lubricating oil range were very unsaturated and contained undesirable substances such as tar acids. A low temperature tar lubricating oil was described a short time ago, but this oil was produced from a bastard cannel coal. No oxidation tests were included in the description of this oil, and the interpretation of the friction tests carried out was not convincing. Hydrogenation, especially in the presence of catalysts, appeared to be a better process for the production of synthetic lubricating oils directly from coal, but no data are yet available as regards temperature viscosity and other relationships of the oils produced. Mr. Minchin raised the question of the ethylation of polymethylenes, and he would say that his colleagues had tried to ethylate some of these by means of ethylene in the presence of aluminium chloride, but so far without success. As regards the oxidation question, this has already been referred

to earlier in the reply. The description of Mr. Nixon's experiments was of interest; as regards the action of selective solvents, experiments on this subject have not yet been attempted owing to the large amount of oil needed for such work.

In conclusion, Professor Nash thanked the members present for their appreciative hearing and valuable discussion, which he felt would prove a great stimulus not only to his colleagues but to all others interested in this subject.

The Chairman, in proposing a vote of thanks to the authors for their very interesting paper, said it dealt with one of those cases where the pure research of the University laboratories promised to be of the utmost value, for it indicated some possible practical outcome; but, as Professor Nash had pointed out in his opening remarks, that development would be left to the commercial and the technical man. He would only say one word of appreciation from the point of view of the academic chemist, namely, that in all probability such work, developed with other gases, might in the long run throw a good deal of light on the nature of petroleum. The question had been put up to Professor Nash as to whether his products compared with this oil or that oil. Surely it could not be expected, from one simple gas like ethylene, to make comparisons between one petroleum and another.

Professor Nash had treated the chemists to a few crystals of hexa-ethyl benzene, but to the chemist's mind there was something a little more than crystals there. They showed the possibility of the production of many other compounds of alicyclic and aromatic hydrocarbons that were likely to be of great interest.

The vote of thanks was carried by acclamation and the meeting terminated.

The Crystallisation of Paraffin Wax.*

By E. Katz.

This work is intended not only to give an exact picture of the crystal forms of paraffin wax, but also to lead to a better knowledge of the crystallisation process. The paraffins on which the observations were made were obtained from Poland and Asia.[1]

Method and Apparatus.

The microscopical researches were made with a Leitz mineralogic microscope on a revolving table, which permitted observations being made in polarised light. The photographs were taken with a common adapter fixed on the tubes of the microscope, in ordinary as well as in polarised light according to the character of the crystal forms to be examined. The enlargement was 260-380.

The substances to be examined were transformed into pure crystals by the cooling of saturated solutions, a close observation being kept while the crystal development was proceeding.

In the first case the technique of the observation was similar to ordinary microscopic investigation. In the second case the apparatus shown in Fig. 1 was employed. This arrangement made it possible to adjust the temperature more easily than by the use of a thermostat and the substance under examination could be transformed from liquid to solid, or vice versa, as often as desired. By this means a large number of observations could be made, and so many photographs taken, that the almost incredible multiplicity of shapes of the crystal-forms which appears at first sight is replaced by a clear perception and their classification made possible.

Preparation of the Material.

The commercial paraffin wax was carefully fractionated by sweating and the researches on the Polish wax were carried out on fractions having the following melting-points: 39° C. (102° F.), 51°–52° C. (125° F.), 56°–58° C. (135° F.), 58°–60° C. (139° F.). In the case of the Asiatic wax the fractions used had melting-points of 50°–51° C. (122° F.), 54°–55° C. (130° F.), 62°–63° C. (145° F.). Tables 1 to 4 show the fractions of the Polish paraffins and their refractive index at 80° C., and a similar table for the Asiatic paraffin is given later in the paper.

* Paper received July 28, 1930.

[1] A product of the Asiatic Petroleum Co., Ltd.

TABLE 1.

Paraffin Wax, M.-Pt. 39·2 °C.

Fraction.	Quantity Gr.	M.-Pt. °C.	n_{80}^{D}
1	5	36·7	1·4261
2	5	37·1	1·4264
3	5	37·7	1·4266
4	5	38·2	1·4269
5	7	40·2	1·4270
6	4	41·8	1·4272
	31		

TABLE 2.

Paraffin Wax, M.-Pt. 50·6 °C.

Fraction.	Quantity Gr.	M.-Pt. °C.	$n_{80.}^{D}$
1	13	45·3	1·4272
2	21	48·0	1·4275
3	12	49·8	1·4276
4	9	51·6	1·4282
5	7	54·9	1·4293
6	6	59·0	1·4299
	68		

TABLE 3.

Paraffin Wax, M.-Pt. 56·6 °C.

Fraction.	Quantity Gr.	M.-Pt. °C.	$n_{80.}^{D}$
1	28	53·1	1·4295
2	9	54·0	1·4297
3	14	56·4	1·4299
4	15	57·5	1·4303
5	13	58·0	1·4304
6	8	58·5	1·4305
7	8	59·5	1·4309
8	7	61·4	1·4311
	102		

TABLE 4.

Paraffin Wax, M.-Pt. 58·8° C.

Fraction.	Quantity Gr.	M.-Pt. °C.	n_{80}^{D}
1	25	57·2	1·4295
2	31	57·6	1·4299
3	24	59·4	1·4301
4	20	59·8	1·4308
5	15	60·0	1·4309
6	13	60·1	1·4310
7	8	60·6	1·4310
8	5	61·3	1·4311
9	6	61·7	1·4311
10	5	62·6	1·4312
11	5	63·7	1·4313
12	3	64·5	1·4313
13	1	65·2	1·4320
	161		

Crystal Forms of Paraffin Wax.

Polish Paraffin Wax.

1. *General.*—A paraffin wax crystal is a very thin plate of different varieties, the original form being a hexagon (Photos 6 and 7a, Plate II.), the angles of which are illustrated in Fig. 2. There are also "needle" crystals which appear in various forms. In addition to these two principal forms there are also the transition forms, the recognition of which is necessary to explain the interdependence of the two chief forms.

2. *Crystallisation in plate form from solutions in kerosine, benzol, etc.*—If a saturated solution of paraffin wax in solvents such as benzine, kerosine, lubricating oil, benzol, carbon disulphide, etc., is prepared at a temperature only a few degrees above ordinary room temperature, and this solution is examined after cooling to a temperature of about 18°—20° C., the separation of the crystals in the plate form can be seen as shown in Photos 1 to 4, Plate. I. In ordinary light these plates look like needles or stafflets,[2] but when a close observation is made in polarised light they are seen as distinct plates with irregular planes in almost invisible forms. This is shown in Photo 3, Plate I., where *a* was observed in common, and *b* in polarised, light. These plates also often appear as twins growing over one another.[3]

[2] D. Vorländer-Selke. Die einachsige Aufrichtung von festen weichen Kristallmassen, 1928.
[3] Tschermak. Mineralogie.

If such a solution is cooled slowly the plates can be seen to enlarge on their planes, forming longish lamells (Photos 1 and 2, Plate I.). Photo 2 was taken twenty minutes after Photo I and the growing of the plates is distinctly seen. If the solution is cooled quickly a thin crystal substance is obtained, as shown in Photo 3, Plate I.

Crystallisation forms of different paraffin waxes from various solutions are illustrated in Photo 4, Plate I.

Generally the crystals are composed of irregular plates, differing even in the size of their planes, as shown in Photos 1 to 4, Plate I.

3. *Crystallisation in plate form from solutions in alcohol, acetic acid, cresol, aniline, etc.*—To obtain well-developed crystals it is necessary to crystallise different fractions of paraffin wax from very dilute solutions, the plates originating well under such conditions. The solvents indicated were alcohol, pure acetic acid, aniline, nitrobenzol, m-cresol, etc., and from these well-developed typical plates, particularly of the high melting-point (about 60° C) waxes, were obtained. With low melting-point (37°—47° C.) waxes, under similar conditions, only thin plates, of irregular and almost imperceptible forms, floating in the original solution, were obtained and were so thin and small that it was practically impossible to prepare them. The forms are not strongly marked, but are only thin foils, sometimes reaching a size of 0·5 sq. cm. or over. In ordinary light they are invisible through a microscope, being only seen by their folds and bends, and are only recognisable when observed in a strong polarised light.

By crystallisation from hydrocarbons it was possible to obtain well-developed plates even from high-melting waxes and, although a thickening means, such as lubricating oil, was added to the solution, the crystals were only very thin and small and hardly visible (Photos 1 to 4, Plate I., and Photo 5, Plate II.). Photo 5 shows the crystallisation of medium-melting wax from kerosine, on an enlargement of 360. The edges of these plates are either even, in rounded forms, as seen in the photographs, or toothed or irregular.

The best crystals were obtained by using dilute solutions of paraffin wax (m.-pt., 60°—65° C.) in 96 per cent. alcohol. Photos 6 to 8, Plate II., show crystals obtained from a saturated alcohol solution at a temperature of about 27°—30° C. In comparison with the solutions used later this was strongly diluted. The hexagons illustrated in Fig. 2 are seen, as well as the characteristic alterations of these crystal forms. Photos 7 and 8 show only the chief forms but many other similar ones were observed. It is probable that the least alteration in the conditions of crystallisation influence the crystal forms, and it is characteristic that the same preparation will give widely different variations. It is not improbable that the

position of the forming crystal in the crystallisation vessel influences the flow of the crystal particles and thus the final form of the crystal. In all cases these researches were carried out with about 50 c.c. of solution. Tanaka, Kobayashi and Ohno[4] obtained similar crystals from shale-oil paraffin and from Japanese petroleum, but obtained rhomboids as well as hexagons, while in the present work only hexagons were observed.

In dealing with the plate form of crystals, their characteristic structure must first be considered. Plates crystallised from alcohol are stratified (Photos 7a and 8, Plate II)., the layers having exactly the same form as the base, and many variations and twins are also found, curiously completing themselves. In Photo 7b, Plate II., it is seen how the single parts of the plate join closely to a hexagon and form two layers, one upon the other, which are easily visible through the thin walls of the plate, while the third layer is placed symmetrically to the axis of the hexagon thus composed. A structure is often seen which is similar to that of starch-flour grains, and it is often observed that the planes of the plate are parallel streaked, similar to the crystal structure known as mimetic, adding streaks one after the other regularly as they develop and grow. Sometimes the streaks change their angles and form edges as illustrated in Fig. 3. In polarised light it is distinctly seen that these parts of the plate are sharply curved, showing that the symmetrical growing of the plate has been disturbed in the crystallisation. Double streaks, running in different directions and looking like a net, are also often seen.

4. *Crystallisation in needle form.*—If the crystal substance from dissolved paraffin wax is put into the same solution as that from which the plates were obtained, at a temperature of 45°—50° C., crystals like needles, and thus so called, are observed. In this case some plates are also seen.

It has been observed that plates are the primary form which may be transformed later into needles. This transformation seems to be irreversible and thus, when favourable conditions for the production of plates as the chief crystallisation form are given, needles are never observed.

The researches were carried out on materials prepared from fully developed crystals obtained by slow or rapid crystallisation from different solutions. The growth and development of the crystals was observed with the apparatus shown in Fig. 1. It appears that the larger the quantity of the solution, and the bigger the crystallisation vessel, the better the crystals develop. A small receptacle

[4] Studies on Crystallation of Paraffin. J. Fac. Eng. Tokyo, 1928, **17**, 275 *J. Inst. Petr. Tech.*, 1929, **15**, Abstr. No. 152.

hinders the crystal development as, although the layers from the same preparation are always thin and small, they develop abnormally and remain unlike the normal crystals.

The researches were first carried out with the above-mentioned apparatus, and in this way it was possible to observe distinctly the beginning and middle stages of the crystallisation. It did not lead, however, especially when using low-melting waxes, to such well-developed crystal forms as when producing them in vessels. The appearance of the needles has been previously described by many investigators, but their explanations differ so much that it is desirable to draw up, after a close observation, an exact picture of the needle type of crystal, as it is too important to be left unexplained.

To understand the origin and structure of needles it is necessary to observe them through all stages of their development. Needles originate from plates, and in the course of this work variations of the needle have been observed in the same way as plate variations were seen previously. Although investigators have, until now, considered needles as characteristic variations of the plates only, the matter is of sufficient importance to point out how they differ from the plates, as well as among themselves, for these variations give proof of the different characteristics of the crystal substances.

5. *Needle development in comparision with plate development.*—In the course of this work it was seen that a paraffin crystal never forms as a needle, but transforms from the plate form to the needle form in the course of crystallisation. *The formation of a needle without development from a plate was never observed.*

Plates are capable of forming spontaneously from paraffin solutions in any solvents, if they are only saturated, and the separation of the particles occurs according to the general rules of crystallisation. The development of needles, however, depends upon the conditions under which the plates form.

As the smallest crystal, that of salt for instance, shows from the beginning of its formation the typical structure of its final form, so the paraffin crystal shows in the beginning the well-developed form of a plate. The author regards the hexagonal form as the base form of the paraffin crystal and the question of the twin form has only been touched on slightly as a mere theory and, for this work, of little importance. The smallest paraffin crystal is in its beginning a plate, it grows as a plate, and it depends on certain conditions whether it remains as a plate or is transformed into the second form, that of a needle.

6. *Crystallisation of pure paraffin during transformation from the liquid to the solid state.—Medium- and high-melting paraffins.*—If

a drop of 58°—60° C. m.-pt. paraffin is placed in the apparatus described and allowed to cool slowly, the following can be observed.

Separation of rounded plates which are entirely flat and float in the current of the cooling substance, appearing, in polarised light, like twisting coins. Although these are forming as round crystals, due to the conditions of high concentration, there is nothing against their being identified as plates. These plates are seen in Photos 9 (right side bottom) and 10, Plate III. This is the first stage of crystallisation.

When the growing plates have attained, in the decreasing temperature, a certain size they begin to bend on their edges and form geometrical figures, such as triangles, etc., and more often hexagons. By this bending sharp emerging ends are formed e.g., the three points in the triangle form. This is the second stage and the forms are to be seen in Photos 9 and 10, Plate III. In these pictures the second stage of crystallisation is a little too far developed as the change to the third stage, even with slow cooling, is very rapid.

Further crystallisation takes place only on the sharp edges of the plates, which do not enlarge, but the edges and points increase and form pointed needles. This is the third stage. (Photo 11., Plate III.)

Needles only are now seen as they entirely cover the plates observed in the first stage. The needles continue to grow, their edges increase and form characteristic points, and just before the temperature of the solution drops at the end of the crystallisation process the appearance of a few plates is again observed (Photos 12, Plate III., 13 and 14, Plate IV.). Thus the fourth and last stage of crystallisation is reached.

It has been seen that the needles are not merely an accidental variation of the plates, but that they develop and grow as independent needles provided that the necessary conditions are given. Of the bending in of the plates only a transition form can arise, and this means a crystal with some points in triangle form, as shown in Fig. 4*a*, *b*, *c*, or possibly the start of the needle form, but never fully developed crystals.

In Photo 49, Plate XIII., the middle stage of the crystallisation of medium-melting paraffin from cresol is illustrated and shows a bent-in plate of triangle form. From the points needles should grow out on further crystallisation, but this did not take place owing to various causes.

From the observation of the growing of the needles it might be expected that, as plates grow by regular and symmetrical addition of particles of paraffin to their planes, so the needles would develop by the addition of particles along the axis of the primary hexagon.

PLATE I.

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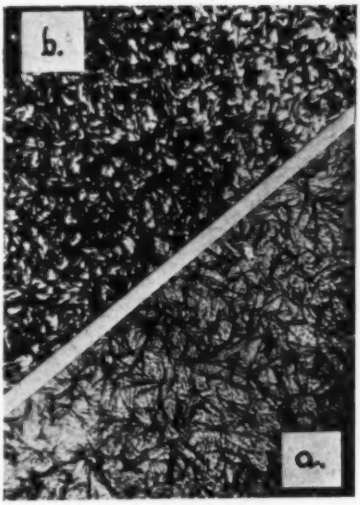

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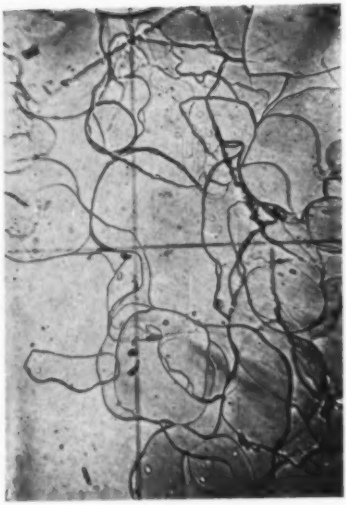
PLATE II.



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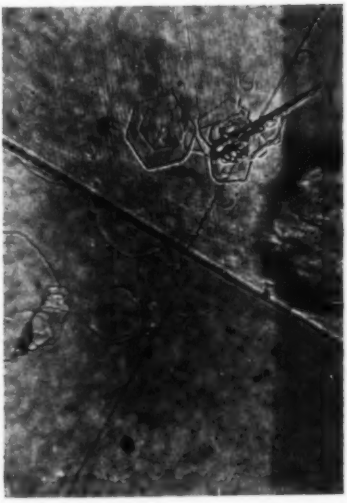

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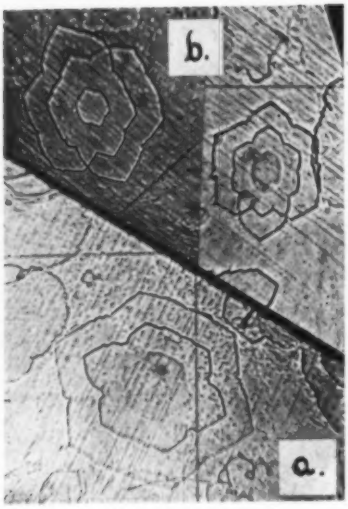

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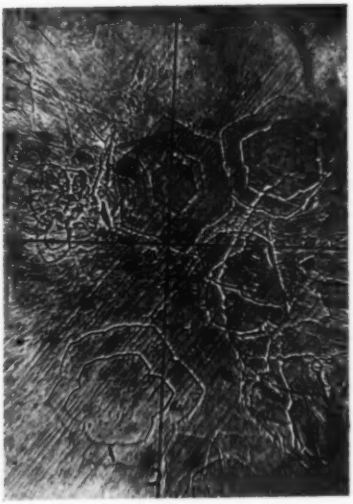

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PLATE III.

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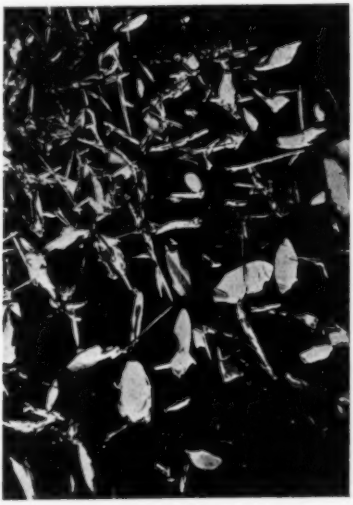

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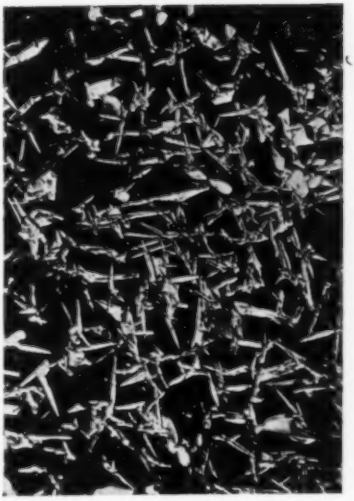

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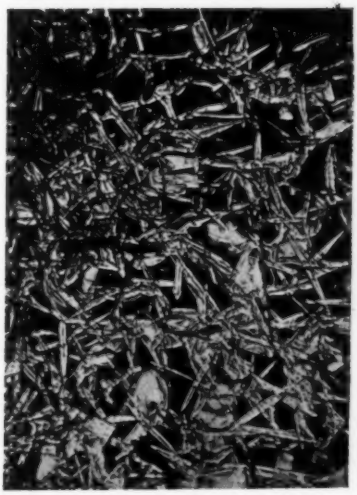

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PLATE IV.

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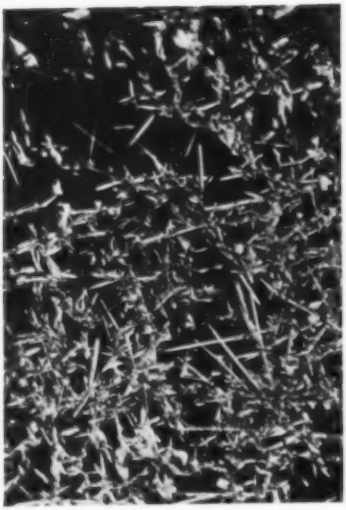

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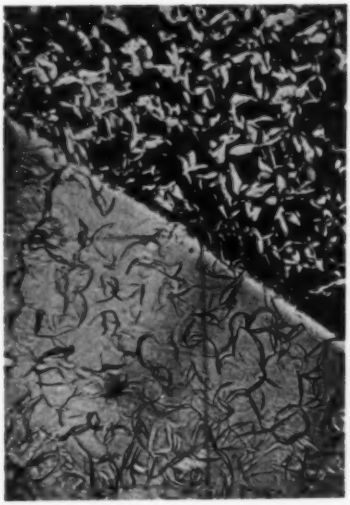
PLATE V.



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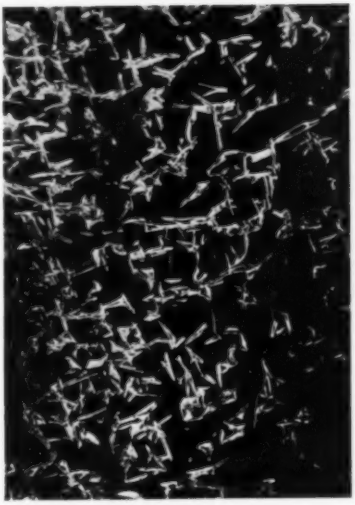

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PLATE VI.

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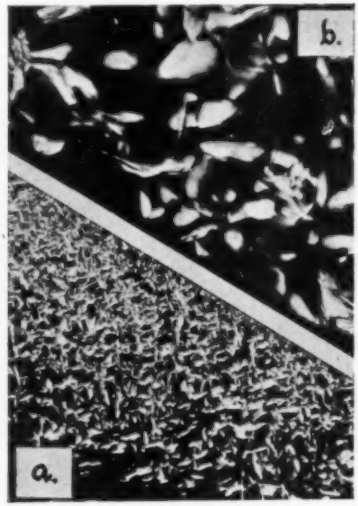

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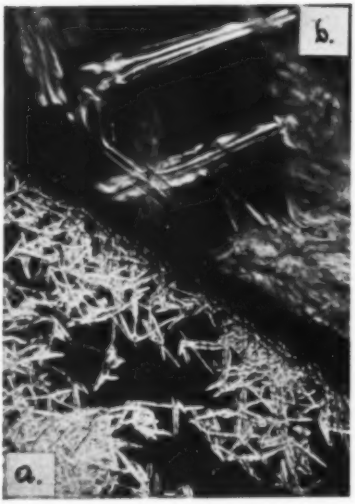

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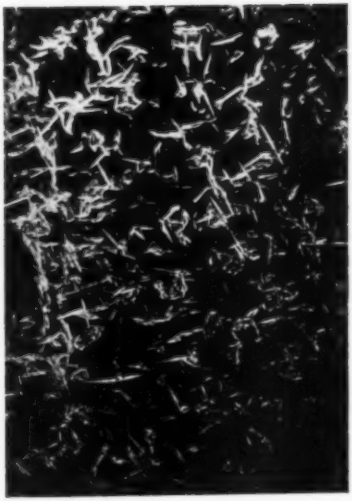

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PLATE VII.

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PLATE VIII.

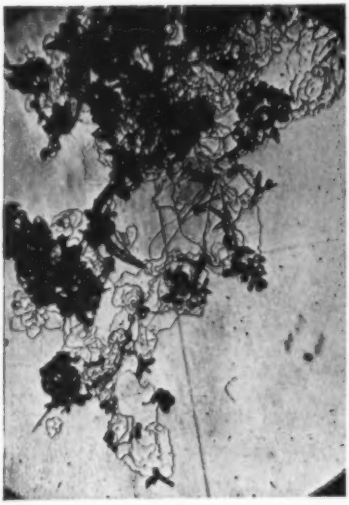

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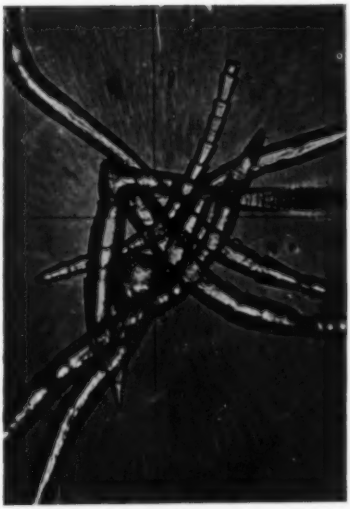
PLATE IX.



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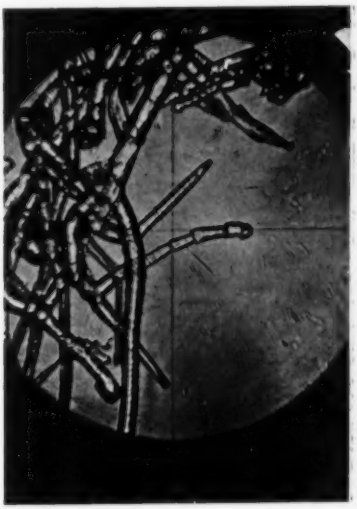

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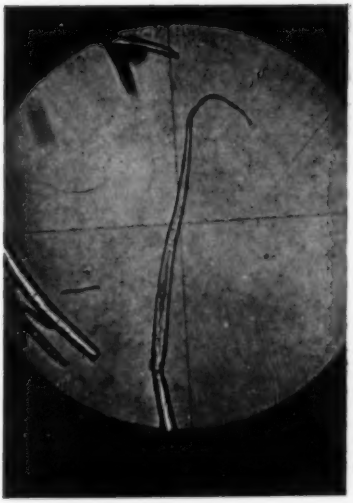

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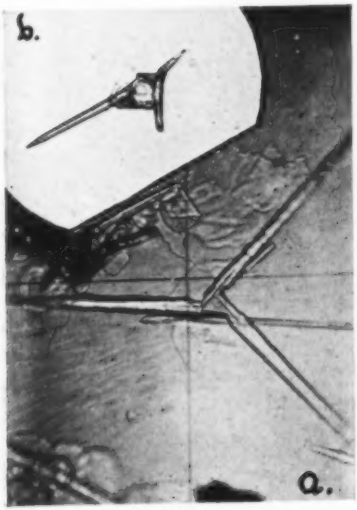
PLATE X.



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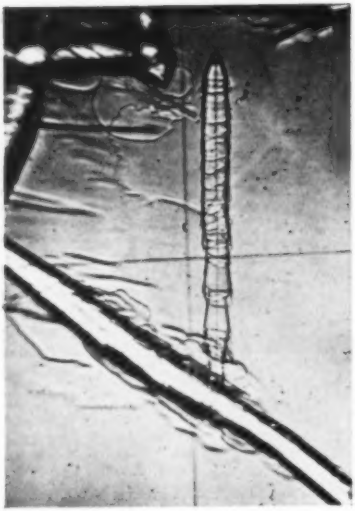

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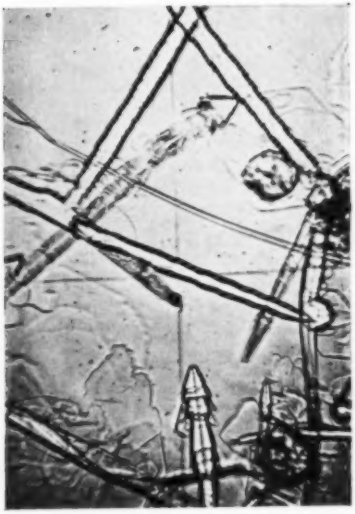

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PLATE XI.

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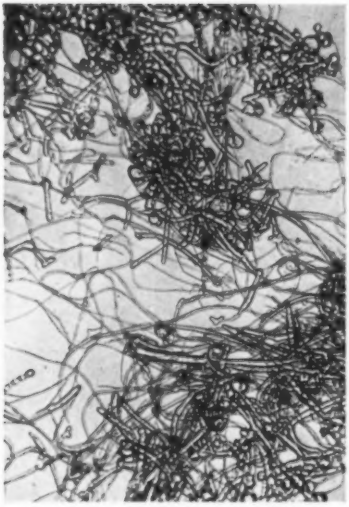
PLATE XII.



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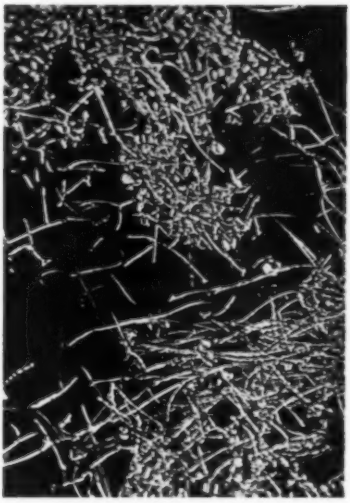

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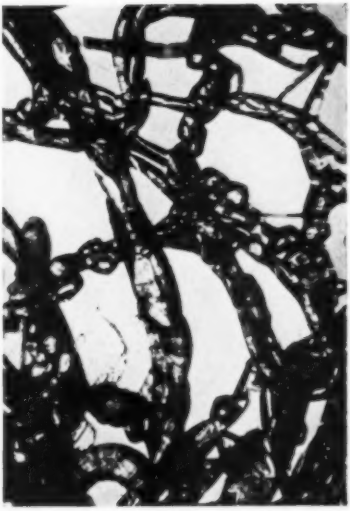

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PLATE XIII.

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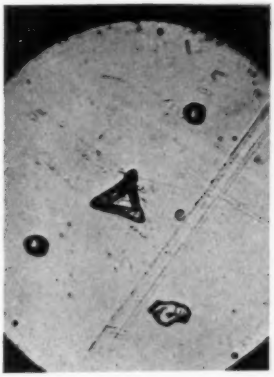

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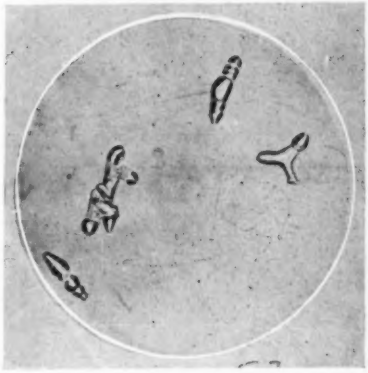

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PLATE XIV.

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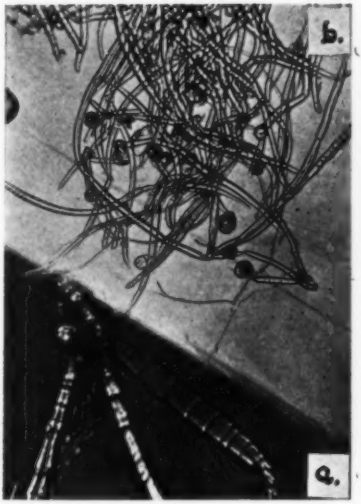
PLATE XV.



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The plates are, however, from their initial stages normal crystals and only grow in size without changing shape, while the needles appear in different forms at different stages in their growth. Further observations showed that needles are only plates not growing in regular planes but in curved ones, out of which sharp pointed staffiets or cylinders are developed (Photo 54, Plate XIII.). Here we have to deal with a distinctly abnormal growth of paraffin crystals. Similar examples are known in other substances and undoubtedly paraffin belongs to that group, the crystallisation of which originates abnormally.[5]

Low-melting paraffin.—The melting-point of low-melting paraffin lies between 37° and 47° C., but the plates have such a great tendency to bending on their planes that it is almost impossible to observe, even with slow cooling, the flat plates which are seen in high-melting paraffins. On further crystallisation the plates are bending in on their edges, forming sharp points out of which long needles are quickly developed. This is shown in Photo 15, Plate IV.

7. *The needle structure of solidified paraffin.*—On breaking a piece of commercial paraffin wax it is possible to see, with the naked eye, the crystals in needle form overlying one another in all directions. This, of course, refers only to paraffin wax obtained by ordinary distillation from paraffin oils. The paraffin wax from high-vacuum distillation, or from residuals, is distinguished by another structure and another course of crystallisation. The crystallisation of normal paraffin wax always takes place in the manner described above and this can be observed, if not with the naked eye, on an enlargement of 250 using a piece of broken, not cut, wax from the middle of the solid mass.

8. *Mottles in commercial paraffin wax.*—It will not be out of place here to discuss the characteristic mottles which appear on blocks of paraffin wax (" mottling "), as by examining this appearance of the structure of the needles is distinctly observed. The causes and conditions from which these mottles arise has already been described,[6] and it is considered that they are caused by air and gases dissolved in the paraffin, and that the more oil the paraffin contains the easier these mottles appear. Photo 16, Plate IV. distinctly shows the nature of this appearance. The " mottle " extends over a certain space perpendicular to the base of the photograph, and what is seen is a cut through a free space in the substance, this space being probably filled with gas or air.

[5] Lehmann. Ueber Wachstum der Kristalle. Z. für Kristallogr., 1877.
[6] J. A. Carpenter. The Physical and Chemical Properties of Paraffin Wax. *J. Inst. Petr. Techn.*, 1926, 12, 288–315.

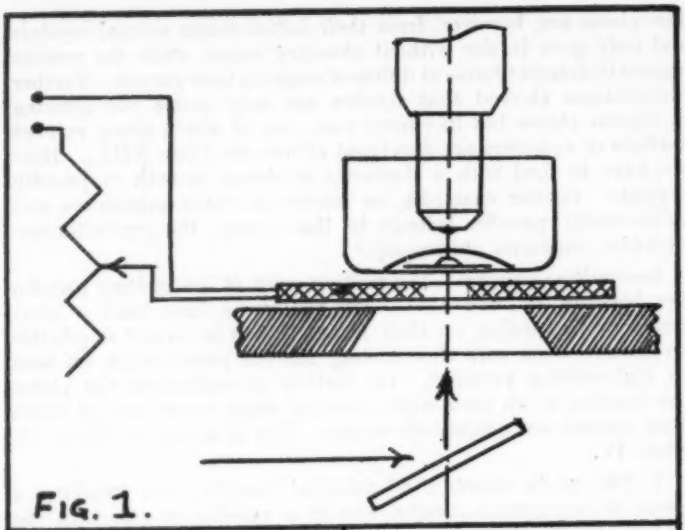

FIG. 1.

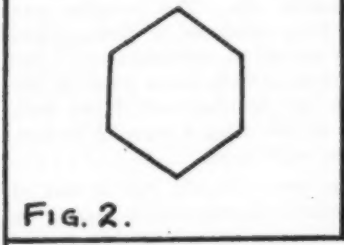

FIG. 2.

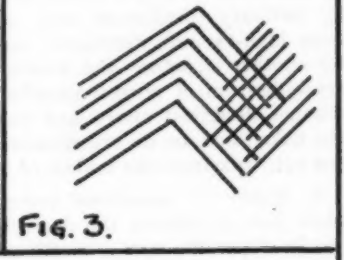

FIG. 3.

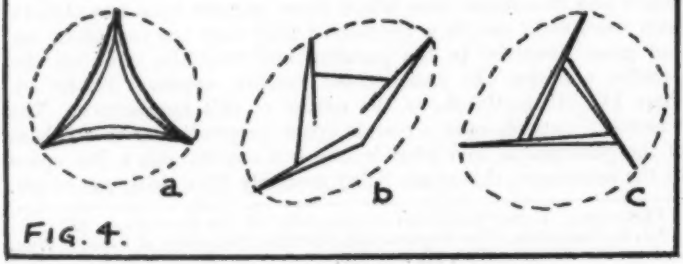

FIG. 4.

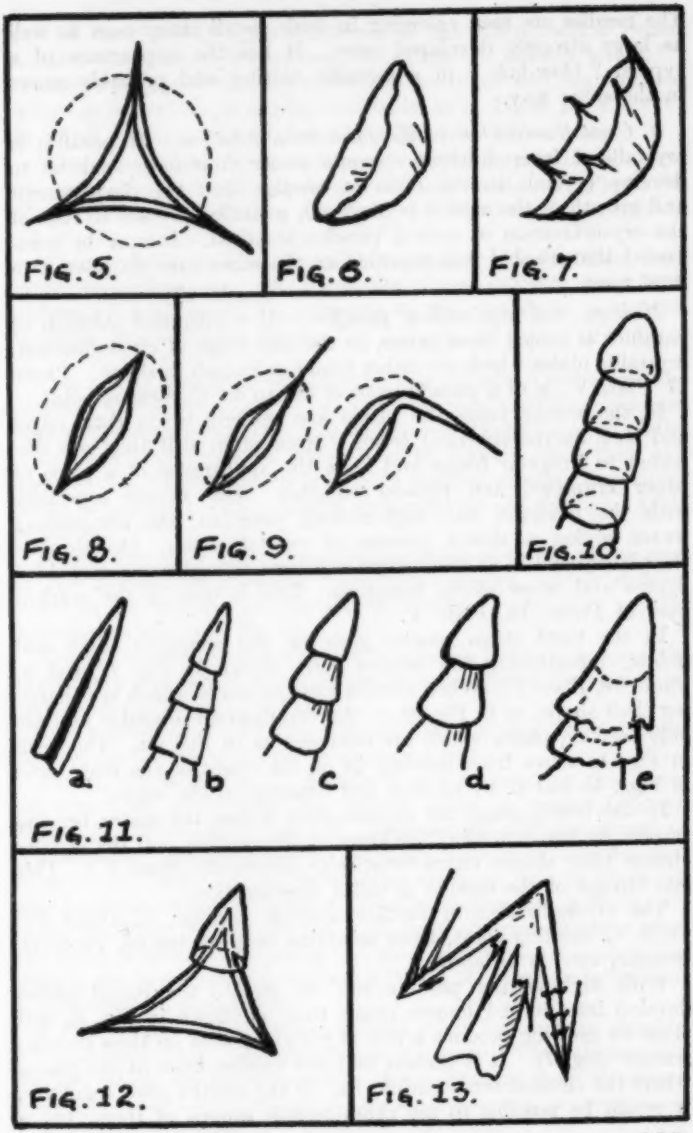

FIG. 5. FIG. 6. FIG. 7.

FIG. 8. FIG. 9. FIG. 10.

FIG. 11.

FIG. 12. FIG. 13.

The needles are seen emerging in buds, small sharp ones as well as large strongly developed ones. It has the appearance of a typical "blow-hole" in a metallic casting and probably arises in the same way.

9. *Crystallisation in needle form from solutions.*—If paraffin is crystallised from different solvents under conditions such as to develop crystals in the form of needles, and the development and growth of the crystal is observed, a similar process to that of the crystallisation of melted paraffin is noted. It may be mentioned that alcohol was regarded as the most suitable solvent in most cases.

Medium- and high-melting paraffins.—If a saturated solution of paraffins is cooled there arises, as the first stage of crystallisation, crystallic plates which are either round or longish in shape. Photo 17, Plate V., is of a paraffin wax of 48° to 49° C. melting point.

In the second stage the plates are bending in on their edges and form curved spherical forms. More often still they are distorted to irregular forms and have the appearance of a piece of paper crumpled and pressed together. This occurs especially with the medium- and high-melting paraffins, the low-melting waxes giving a slower process of crystallisation. Occasionally the plates bend in on their edges and form triangles or many-sided figures and, more often, hexagons. This is seen in the marked part of Photo 18, Plate V.

In the third stage needles grow on the emerging edges and points, maintaining the bended form shown in Fig. 5, and in Photo 18, Plate V. When needles form on plates which are changing their shape, as in Fig. 4*b*, *c*, the bendings are invisible and are only seen on plates which are changing as in Fig. 4*a*. The form in Fig. 4*a* arises from bending in on the edges of the plate, and in Figs. 4*b* and 4*c* by rending and bending on the edges.

In the fourth stage the needles grow larger, the plates become smaller by the increasing thickness of the needles, and the needles change their shapes characteristically (Photo 20, Plate V.). This last change of the needles is called degeneration.

The crystallisation of medium-melting paraffin, of about 48° to 55° C. melting point, from solutions such as benzol, kerosine, benzine, etc., is as above.

With high-melting paraffin (55° to 65° C.) the round plates develop into curved figures (stage two) as shown in Fig. 6, and these on growing produce a row of rib-like points on their circumference (Fig. 7). It is certain that the needles grow at the places where the circumference shrinks in. If the needles grew regularly, it would be possible to see characteristic groups of them, but a

few of them grow to the detriment of the others, which remain small to the end of the process. This effect is already known.[7]

The final aspect of the crystallised medium- and high-melting waxes is in both cases similar and looks as in Photo 20, Plate V., in which is seen a chaotic heaping of the needles.

When crystallised from lubricating oils the needles do not grow so large as when light hydrocarbons are used, and Photo 19, Plate V., shows medium paraffin crystallised from automobile oil of 13½° Engler viscosity at 50° C.

When medium- and high-melting paraffin is crystallised from larger quantities—*e.g.*, 50 c.c.—of the above solvents, only little differences are seen in the structure of the crystals in proportion to those obtained from drops.

Low-melting paraffin.—The paraffin wax examined had a melting-point of about 37° to 47° C., and when crystallised from solvents such as kerosine gave, in the first stage, round, lightly curved plates.

In the second stage the plates bend in entirely along their axis and not only at the edges as with high-melting paraffin, developing forms as in Fig. 8. This stage is similar to the cut through a grain of barley.

During the third stage the growth continues on the sharp ends of the plates, transforming them into needles, which develop either in the direction of the axis of the bent plate or in another direction as shown in Fig. 9.

Finally, a mass consisting chiefly of single crystals is seen, the appearance of which is explained as above as against the heaped-up needles of high-melting paraffin.

The crystallisation of low-melting paraffin wax from viscous lubricating oil occurs almost in the same way.

As this development of crystals is not so good as that from solutions such as kerosine, the process is not so easily observed. Photos 21, 22 and 24, Plate VI., illustrate the different stages of crystallisation from automobile oil when a drop of this solution is used. In Photo 21 the little plates are seen, and in Photo 22 they begin to bend in to develop into the needles seen in Photo 24. Photo 23, Plate VI., shows the final stage of crystallisation from the same solution, but using 50 c.c., and it is seen that the crystals are better developed than in Photo 24, drop crystallisation, (a = ca 280x; b = ca 380x).

A still greater difference is observed when low-melting paraffin is crystallised from solvents of low viscosity. Crystals are developed which are entirely unlike those obtained from the same

[7] Lehmann, Kristallanalyse: Tschermak, Mineralogie.

solution in drops and cooled at the same rate. Photos 25 and 27, Plate VII., show the final stage of crystallisation of 39° C. melting-point paraffin wax from petroleum in a 50 c.c. solution, while Photo 28, Plate VII., shows the same when observed microscopically during the cooling of a drop on a glass.

Previous researches, based chiefly on drop crystallisation, do not show distinctly these characteristic forms, particularly with the low-melting paraffins. In this work the differences between crystallisation from drops and from larger quantities have been recognised and give a true picture of paraffin wax crystallisation.

10. *Different kinds of needles and their structure.*—Saturated solutions in alcohol were used, the crystals obtained showing very well all the characteristics of well-developed paraffin crystals, while the small quantities of solution facilitated the observation. Acetic acid, butanon, etc., also behave similarly, and observations were also made on solutions in aniline, m-cresol and nitro-benzol, although with the latter the crystals did not develop as well as from alcohol.

If a saturated solution of paraffin (about 50° C. m.-pt.) in alcohol is cooled to room temperature and the resulting substance observed in a microscope, the upper layer of the cooled, but not mixed, solution will be seen as in Photos 29 (ca 250x) and 30, (ca 360x) Plate VIII. If the lower layer is similarly observed then the characteristic forms shown in Photos 31 and 32, Plate VIII., will be seen. Similar crystal forms are obtained if a saturated solution of paraffin in alcohol is cooled to 25° C. and the crystal substance quickly separated by filtration from the remaining solution while maintaining the temperature constant. The separated crystal substance appears as entangled needles as in Photo 31, but the remaining solution, when cooled to about 18° C., gives further separation of dissolved paraffin which, observed microscopically, looks like Photos 29 and 31, Plate VIII. The explanation of this is that the paraffin wax separating from a saturated alcohol solution at the higher temperatures (45°—50° C.) is in the form of needles, but from very dilute solutions at low temperatures (20°—22° C.) plates are obtained. Therefore, preformed needles, which have sunk to the bottom of the vessel as an entangled mass, are found while the plates formed at the lower temperature have also been separated. By such fractional crystallisation the two states can be practically separated. The plates may be mixed with a few needles but the question of form is only one of dilution of the substance, or one of crystallisation at a lower temperature. By using sufficiently dilute solutions needles only are obtained.

Medium-melting paraffin.—Photos 33 to 36, Plate IX., show needle crystals of paraffin fractions of 50° C. m.-pt. obtained from a saturated alcohol solution. Characteristic variations are seen, some being even (Photos 33 and 36), some showing a compound structure (Photos 33 and 34), while others show a layer construction (Photo 35), although the single parts are not well seen.

These needles must be obtained between those of low- and high-melting paraffins.

High-melting paraffin.—The needles of high-melting paraffin are better than those of low-melting paraffin for the examination of the needle construction on account of their being harder. Photo 37*a*, Plate X., shows a three-armed needle enlarged 360 times and the remainder of the plate from which the needle arose can be distinctly seen. The plate has bent in and formed sharp points as illustrated in Fig. 4. A similar picture of the needles in Photo 37*a* is given in Photo 37*b*, Plate X., which shows an earlier stage, the needles being even and still growing. Here, too, the remainder of the plate is visible. Photos 38 to 40, Plate X., show the single arms of the many-armed needles, and the layer structure can be seen.

These needles appear to be composed of little sets which, being transparent, are very well observed. The needle points are seen on Photo 40, Plate X., on an enlargement of 360.

A complete explanation of all these forms gives Photo 41, Plate XI. During this work it was observed that needles, on being partly crumpled between two glasses, changed their forms in a very characteristic way. Photos 41 to 43, Plate XI., show the partly deformed needles obtained by gentle pressure on the preparate of the normal needles seen in Photos 37 to 40, Plate X. The construction of needles composed of layers is now understood and consists of single small layers, one upon another, as in Fig. 10. In Photos 34 and 35, Plate IX., is seen a needle deformed as above, and which before deformation looked like a needle seen in Photo 27, Plate VII. After pressure, layers were seen which had previously formed rings round the needle. This is seen more clearly in Photo 43, Plate XI., which shows the strong connection between these layers and rings. Here is seen a typical deformed needle which has lost its normal jointing in the pressure and separated into single parts which appear as characteristically built sets.

This articulated structure can be distinctly seen in Photo 44, Plate XI., which shows a needle from which a few of the funnel-like layers have been cut off, while the rings and layers of the remaining part are still clearly visible, especially in the upper part.

In view of all these observations it can be said that *the needle crystal is not a homogeneous body, but on the contrary is built up of conglomerated particles which form jointly the rather complicated needlebody.*

This recalls the arising of individuals of the lower class of compounded crystals. The jointed conglomerate represents the type of the higher class, known in mineralogy as "mimetic crystals." The construction of needles from medium-melting paraffin wax could not be examined in this way, as these, owing to their softness, formed a shapeless mass under the least pressure. General observation of the needles from this paraffin is sufficient to ascertain that they are entirely analogous. (Photos 33 to 35, Plate IX.)

Low-melting paraffin.—Looking at Photos 45 to 48, Plate XII., it is seen that the crystals are not entirely similar to the needles described above. With similar crystals the process of crystallisation of low-melting paraffin from petroleum was described, Photos 25 to 27, Plate VII., but the special characteristics in structure were not shown to such a degree. These are needles of low-melting paraffin, 37° C., crystallised from a saturated alcohol solution, and appear as long thin stalks not at all like the conglomerated needles. A few of the conglomerated needles are seen in Photo 45, Plate XII., as this was taken during a rapid cooling, while Photo 47, Plate XII., taken during slow cooling, show no such crystals. These needles are, however, only slightly different in construction from those of high-melting paraffin, although from their external appearance they seem to vary greatly.

The solution of this problem is facilitated by crystallisation from drops.

The long, even needles seen in Photos 45 to 48, Plate XII., probably arose in the same way as in the high-melting paraffin except that the single layers, under certain conditions, arranged themselves in a different way and thus formed a characteristic needle. This type could be regarded as an independent needle, but that it is not so is seen on crystallisation from a drop. This is clearly shown by comparison of crystals obtained from drops and from larger quantities (Photos 25 to 27, Plate VII.) of the same solution. The last photographs show even needles like those obtained from alcohol solutions, but the points show distinct layers, thus proving the layer construction of the whole, as it is hardly possible that a needle begins to crystallise in one way and finishes in another.

The course of the degeneration is shown in Fig. 11*a*, in which is seen an even, straight needle which grew on the emerging point of the plate. After a time this becomes characteristically toothed and covers itself with layers, as in Fig. 11*b*. These layers grow and thicken at their edges, giving the forms shown in Figs. 11*c* and

11*d*, and continue to grow, forming the strongly-marked rings best seen in Photo 33, Plate IX. Some of the rings grow on as more or less thin plate walls, Fig. 11*e*. There sometimes arises, chiefly at the end of the crystallisation, buds of these layers which then change into plates (Photo 40, Plate X.), and in this interesting appearance great varieties are observed. Sometimes the needles grow to the stage shown in Fig. 11*e*, while others remain with one or two rings concentric to the points of the needles and hindering the further development. This is seen in Photo 18, Plate V., and in Fig. 12. Photos 53 and 54, Plate XIII., show two examples of similar crystal growth in needle form in paraffin of 50° C. m.-pt. from m-cresol. New needles sometimes arise on the single layers of the primary needle which grow in opposite directions. These grow and cover themselves with new plates, giving the tertiary form of needle, Fig. 13. The further observation is difficult on account of the great accumulation of needles, but there is nothing against the supposition that this process continues to repeat itself in a similar way to the so-called "skeleton growth of crystals." [8]

In general, in paraffin an inclination to the skeleton growth of its crystals is observed.

Summarising these observations it may be said that the needle grows by the settling of the layers one upon another, each layer having the characteristic shape of a funnel. In the beginning the layers are very thin and the edges are not seen but only leave an irregularity on the needle which later develops and marks out the layers. The layers increase their forms during crystallisation and form characteristic bodies as seen in Plates IX. and X., and in Photos 53 and 54, Plate XIII.

The changes described above have been noted in the crystallisation of both the medium- and high-melting paraffin waxes, irrespective of whether drops or larger quantities were used, but are never met when crystallising low-melting paraffin from alcohol in larger quantities. From this latter only long stafflets were obtained which, even on enlargement, showed no signs of layers. When these waxes are crystallised from drops the layer construction is seen and, further, solutions in, *e.g.*, kerosine, give crystals the points of which have a clear layer construction, and it must be assumed that the crystals of low-melting paraffin have in general a layer construction also. The layers doubtless have a more normal, and thus less visible, shape and cover themselves along the whole length of the needle. This can be seen in Photo 26, Plate VII.

The fact that it was not possible to observe the long, even needles when low-melting paraffin was crystallised from a drop proves that those changes called degeneration are only a normal crystal growth.

[8] Lehmann. Kristallanalyse.

The crystals of medium- and high-melting paraffin pass through all the stages of crystallisation and change in the last stage into degenerated forms, and this proves that their crystallisation, though affected by such particular conditions as slow cooling, etc., is less normal than that of low-melting paraffin. This is probably due to conditions of over-cooling or of over-saturation, which are more common with the high- than the low-melting paraffin waxes. This is supported by the fact that a solution of 37° C. m.-pt. in alcohol, when rapidly cooled, gives in addition to the long, hairy needles a few conglomerated ones (Photo 45, Plate XII.). On slow cooling, however, this solution only gives the first forms (Photos 47 and 48, Plate XII.).

11. *Transition crystals.*—It still remains to mention the crystals between the plate and needle forms. Photo 49, Plate XIII., shows in polarised light a deformed plate giving the base for the formation of needles which were retarded in their development by uncontrollable circumstances. Photo 50, Plate XIII., shows a plate so deformed as to be bent in externally as well as internally. It is probable that this plate cracked and took a triangular shape at the points of which characteristic sets arose. In Photos 51 and 52, Plate XIII., are seen needle forms of 51° C. m.-pt. paraffin crystallised from cresol showing characteristic points. Photo 55, Plate XIV., shows the uncompleted growth of crystals of low-melting (38° C.) paraffin from alcohol, and Photo 55*a* shows a needle which arose from a plate, the clear parting of which proves the cause of its formation. It is characteristic that the plate, which at one part gave the base for the formation of the needle, remained in the form of a plate combined with a needle until the end of the crystallisation. Photos 55 b. and 55c. show similar forms (55b in polarised light), but here the plates are seen changing into two needles. Photo 56, Plate XIV., shows in polarised light not only a long, even needle constructed in layers, but also a short, partly developed needle (paraffin and solution as above). Photos 57 and 58, Plate XIV., illustrate the transition form between plate and needle in the crystallisation of low-melting (39° C.) paraffin from alcohol. Plates are seen, however, which did not undergo the normal bending in, but thickened and gave characteristic forms mostly with thickened points.

Asiatic Paraffin Wax.

A few kinds of Asiatic paraffin were examined under similar conditions to the foregoing, the samples used having melting-points as follows: 122° F. (50°–52° C.), 127° F. (54°—56° C.), 143° F. (62°—63° C.).

The 122° F. m.-pt. wax was fractionated by sweating, and the properties of the fractions are given in Table 5.

TABLE 5.

Paraffin Wax, M.-Pt. 50° C.

Fraction.	Quantity Gr.	M.-Pt. °C.	n_{D}^{80}
1	32	47·7	1·4267
2	20	48·3	1·4270
3	18	49·0	1·4274
4	15	49·6	1·4276
5	20	50·6	1·4280
6	18	51·2	1·4282
7	21	52·0	1·4284
8	20	52·8	1·4286
9	22	54·0	1·4287
10	9	54·6	1·4289
11	7	55·8	1·4290
12	9	58·0	1·4291
	211		

It was observed that the crystallisation of the medium- and high-melting Asiatic paraffins occurred in a similar manner to that of the Polish paraffins. Low-melting Asiatic paraffins were not available, so that no comparisons were possible for these.

Photos 59 to 62, Plates XV., show characteristic crystal forms of the crystallisation of Asiatic paraffin; Photo 59, medium-melting, and Photos 60 and 61, high-melting, paraffins from solutions, and Photo 62, the needle structure of solidified paraffin.

Conclusions.

It was necessary to devise special research methods to obtain all the observations, and it was often necessary to depart from the proper theme in order to study the growth and the different forms of paraffin crystals. Considering all the observations it can be said :

The paraffin crystal is a six-sided plate which is most probably a many-folded twin, as proved by the characteristic bendings and shapes. The plates show clearly a layer construction and, under certain conditions, deform to a form between the plate and needle, this form being the base for the growth of the needle.

The formation of a needle must be preceded by a plate, and several needles can arise from one plate, the number depending on the deformation of the plate.

The needles are only plates characteristically formed in layers so that the general aspect gives the picture of a needle.

Low-melting paraffin wax gives other forms in which are observed long, even needles without a visible layer surface, but a

closer examination shows that these needles also have a layer construction.

The needle is not a homogeneous crystal but is a conglomerated one. It arises in the abnormal course of crystallisation, which can be controlled by varying conditions and which will be dealt with in a later work.

The so-called degeneration is only a further degree of the abnormal paraffin crystallisation. The rings which form at the points of the needles probably hinder their further growth.

The growth of secondary and tertiary needles is a known appearance and often occurs in the crystallisation of bodies such as snow crystals.

The degeneration and growth of needle crystals can be controlled under the conditions which generally form the base of the skeleton construction.

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Geothermal Phenomena and Geological History with Special Reference to Old Structures in Geothermal Equilibrium.*

By M. W. Strong.

1. *Introduction.*—Some 75 years ago Lord Kelvin advocated special geothermic surveys as a means of estimating absolute dates in geology. With the late revival of interest in the subject and the consequent increase of data, the achievement of this object, in the case of young structures, seems appreciably nearer. There is also considerable evidence that geothermal irregularities often shed light on geological history in the case of older structures; and conversely, when this history is known, it may be of great help in elucidating complicated geothermal data.

Rocks are bad conductors of heat, and disturbances of geothermal equilibrium due to climatic, physiographic, tectonic, volcanic and other causes, may take long periods of time to die away. Especially in the case of some major-Pliocene and post-Pliocene disturbances is there strong evidence that the present geothermal distribution is not in equilibrium with the present conditions.

We shall first consider the thermal conditions to be expected in old structures. Investigation is continuing with reference to these conditions in young structures where thermal changes may be expected to be still continuing.

2. *Some Factors Affecting Geothermal Distribution.*—In structures sufficiently old for geothermal equilibrium to have been established, the conductivities of the rocks and their fluid contents must usually be the dominant factors determining the thermal conditions. In rocks that are thermally homogeneous the isogeotherms will, if the surface is level, be dependent mainly on the depth and independent of the inclination of the strata except in so far as the conductivities of the strata are functions of their inclination.

Generally, however, there are topographic irregularities which must be taken into consideration. Effects due to underground movements of water, oil and gas, cannot be treated in a general manner, and must be analysed specifically in each case in which they arise.

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3. *Conductivities of Rocks.*—The following are some representative approximate conductivities of rocks and various substances of importance in the following discussion :—

	Conductivity C.G.S. units.
Soil (clay or sand), damp	0·0037
Sandstone	0·005
Limestone	0·005
Granite	0·0081
Coal	0·0008
Rock salt	0·016
Iron	0·14
Petroleum	0·0003
Water	0·00143

4. *Influence of Thermal Conductivity on Strata on Isogeotherms.*—It is of interest to examine by the aid of some well-known diagrams the distribution of heat in and around masses of relatively good and bad thermal conductivity placed in a medium through which heat is flowing.

In the steady outflow of heat towards the surface of the earth, rocks of low conducitvity will tend to retard the flow and rocks of high conductivity to accelerate it. The temperature gradient, varying inversely as the conductivity, will be high through bad conductors and low through good conductors, as illustrated in Figs. 1 and 2.

Now in Fig. 1, suppose the upper half of the diagram removed so as to bring the central and straight isogeotherm AB to the surface, maintaining the layer represented by that line at the same temperature as before. It is clear that the equilibrium of the thermal distribution represented by the lower portion of the diagram will remain undisturbed. By removing the upper portion part of the badly conducting body is exposed and the temperature distribution is now as in Fig. 3.

This figure shows the distribution to be expected, for instance, in the case of an outlier of limestone or sandstone on a mass of saliferous shales.

Similarly, in Fig. 2, consider the isogeotherm CD as representing the surface of the ground : provided the temperature remains unaltered, equilibrium conditions will be undisturbed, and the temperature distribution will be as shown in Fig. 4.

An outlier of saliferous shales resting on limestones or sandstones would give this type of distribution. An old exposed salt dome should also show similar depression of the isotherms.

Examples of masses of material of high thermal conductivity are salt domes, sediments impregnated with salt, and metallic ore bodies ; while among poorly conducting materials are coal

seams, oil shales, and probably (though this needs investigation) fine clays and plastic damp clays.

From the foregoing it is clear that the influence of any given geological body on the geothermal gradient varies with its distance from the surface. Thus an old salt dome exposed at the surface should have a depressing effect, and old salt mass still buried an elevating effect on the isogeotherms around the upper portion.

5. *Buried Hills or Anticlinal Structures.*—We consider next buried hills and anticlinal structures, supposing in each case that the structure is old enough for geothermal equilibrium to have been attained.

The geothermal distribution to be expected in the neighbourhood of a buried hill of low conductivity covered by a mass of sediments of higher conductivity is shown in Fig. 1, from which figure it will be seen that in and around the upper part of a buried mass of relatively low conductivity the isogeotherms will be depressed, but below a certain depth they will be raised in and around the same mass. Whether these phenomena occur or not will depend on the size of the mass and the difference between its conductivity and that of the surrounding medium.

In the case of a buried mass of relatively high conductivity, as shown in Fig. 2, an opposite effect on the displacement of the isogeotherms will be observed.

6. *Faults and Unconformities.*—Consider next the distribution of isogeotherms in the neighbourhood of a fault which has thrown badly conducting strata against strata of higher conductivity. The gradient will be low in the good conductor and high in the poor conductor, and the differences of temperatures between strata on either side of the fault plane increases with the depth.

In the case of a fault of high hade we have to consider two cases (Figs. 6 and 7).

The relatively bad conductor may be underneath or may overlie the better conductor. These figures may be taken as illustrating also the conditions arising in the case of an unconformity, the plane of which is dipping slightly. An identical condition also arises where exposed and tilted strata, though conformable, contain thick beds of differing conductivity, *e.g.*, a gentle monocline with a thick coal-bearing formation covered by better-conducting strata. This point might be considered in connection with the depression of thermal contours in the Permian basins of Oklahoma and West Texas, where the underlying poorly conducting limestones are covered by Permian Red Beds, which are in places saliferous.

Consideration of Fig. 6 shows that as we proceed down the plane separating the two types of strata, the scale of the effect becomes

larger, tending to increase linearly with the depth. Such thermal conditions are to be expected where limestone strata dip beneath saliferous strata. If the limestone strata were above the conditions would be as shown in Fig. 7.

Consideration of Fig. 7 shows that the deeper we proceed down the plane of separation of the two different strata the greater are the distances from the plane of discontinuity at which the thermal effect is measurable. Given an isogeotherm determined at a particular depth, that at twice the depth may be approximately deduced by doubling the scale of the first, provided the stratigraphic conditions are similar.

By a combination of Figs. 1 and 6 an interesting example of the thermal distribution associated with a compound limestone structure partly buried under a saliferous series is obtained, as shown in Fig. 8.

In Fig. 8 it will be noticed that an abnormal depression of the isogeotherms is noticeable round the crestal portion of the buried structure. In the deeper portions the isogeotherms fall from right to left, the changes of inclination due to the buried structure decreasing with the depth. An extension of this figure to the left with other and deeper structures coming in might exemplify the conditions found in the Permian basin of Oklahoma.

7. *Buried Faults and Unconformities.*—We may next consider the thermal distribution above a buried fault by which beds of different conductivities have been brought into contact, the whole lying buried beneath a thick overburden.

For high-hade faults buried under later strata and also for buried unconformities we obtain Figs. 10 and 11.

If the lower strata had been irregularly denuded and folded before being covered by the later beds the figures already given indicate the type of irregularities to be expected.

Some Oklahoma fields, *e.g.*, Tonkawa, should be of interest in this connection, with its irregularly eroded Mississippi limestone overlying the Wilcox sand.

8. *Importance of Conductivity Determination.*—From a study of the diagrams it will be seen that in old structures, in which for all practical purposes geothermal equilibrium may be considered as established, the conductivities of the different strata would be one of the controlling factors determining the geothermal distribution.

It is important, therefore, that the determination of the conductivities of the beds should be one of the first objectives of a geothermal survey. The diagrams show that owing to local distortion of the thermal field the gradients in given localities are

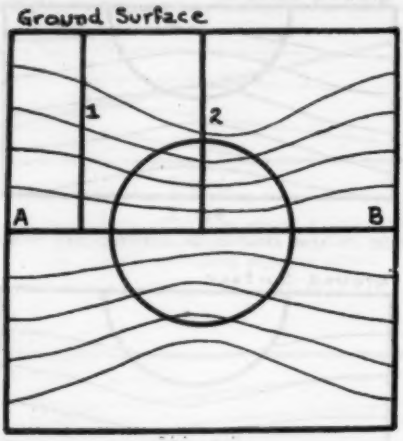


FIG. 1.

ISOTHERMS IN NEIGHBOURHOOD OF BURIED MASS OF BADLY CONDUCTING MATERIAL.

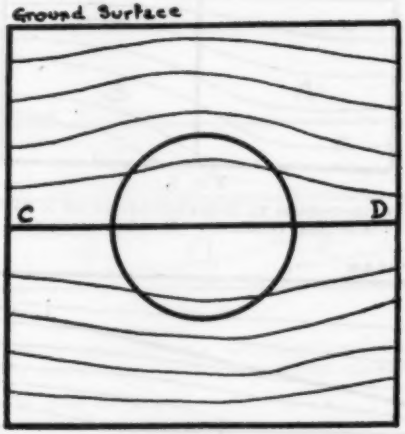


FIG. 2.

ISOTHERMS IN NEIGHBOURHOOD OF BURIED MASS OF HIGHLY CONDUCTING MATERIAL.

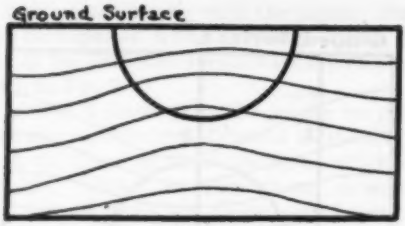


FIG. 3.

RAISED ISOTHERMS IN AND AROUND AN EXPOSED BAD CONDUCTOR.

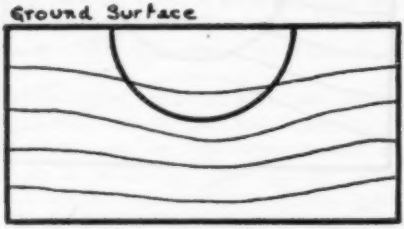


FIG. 4.

LOWERED ISOTHERMS IN AND AROUND AN EXPOSED GOOD CONDUCTOR.

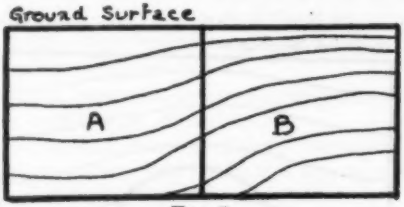


FIG. 5.

ISOGEOTHERMS IN NEIGHBOURHOOD OF A FAULT.
A = good conductor. B = bad conductor.

FIG. 6.

ISOGEOTHERMS IN NEIGHBOURHOOD OF A LOW ANGLE FAULT WHERE BADLY CONDUCTING STRATA ARE BELOW.
AB = plane separating different strata.

FIG. 7.

ISOTHERMS IN NEIGHBOURHOOD OF A LOW ANGLE FAULT WHERE BADLY CONDUCTING STRATA ARE ABOVE.
AB = plane separating different strata.

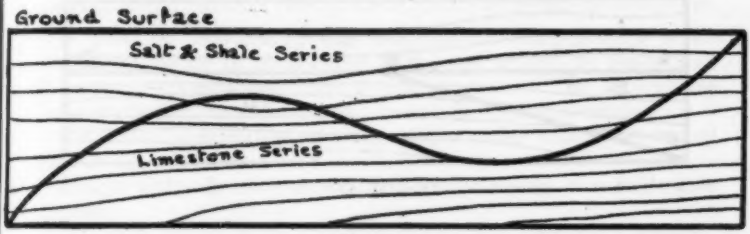


FIG. 8.

ISOTHERMS IN RELATION TO A COMPOUND LIMESTONE STRUCTURE.

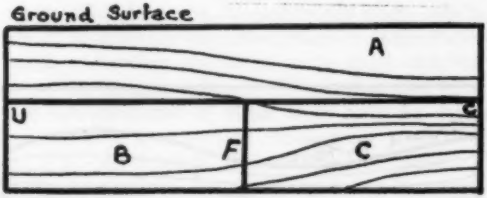
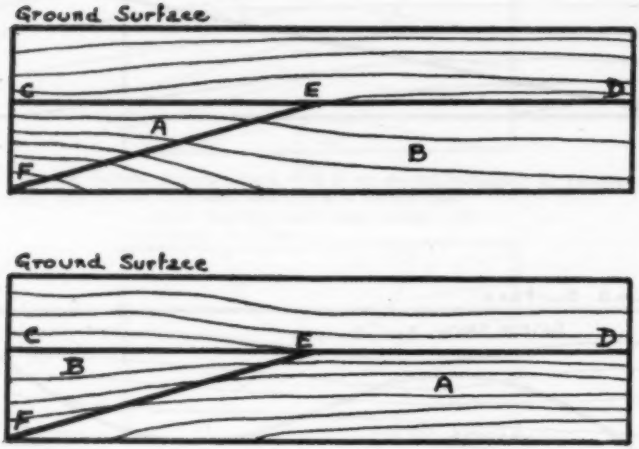


FIG. 9.

ISOTHERMAL LINES IN THE CASE OF A MODERATE CONDUCTOR COVERING A GOOD AND A BAD CONDUCTOR FAULTED TOGETHER.

A = Beds of moderate conductivity.
B = Beds of high conductivity.
C = Beds of low conductivity.
U—C = Plane of unconformity.
F = Fault plane.



FIGS. 10 AND 11.

ISOTHERMS IN RELATION TO A BURIED UNCONFORMITY OR THRUST.

CED and FE = Planes separating various strata.
Beds above CD of average conductivity.
A = Beds of low conductivity.
B = Beds of high conductivity.

FIG. 12.

ISOTHERMAL CONTOURS IN EQUILIBRIUM UNDER HILLS.

generally insufficient for determining this constant, though they give valuable comparative data. This point is discussed in detail in the section on gradients.

In Lord Kelvin's "Mathematical Physical Paper," Vol. III., will be found a full account of the use of the annual range of temperature at various depths, for computing the conductivity of strata.

The diurnal waves cannot be relied upon for conductivity experiments owing to their small depth of penetration, combined with local irregularities of the soil and drainage. Studies of the temperatures at the surface are, however, invaluable in providing a check on all measurements in the district, for the depth-temperature curve for any bore-hole, putting aside accidental causes, should intersect the surface at the mean surface-temperature.

9. *Note on Topography and Isogeotherms.*—Topography is an important factor in geothermal work, and should be taken into account in constructing underground contours. The subject has been studied in detail by Stapff, Prestwich, Lees and others.

The static distribution of temperature under hills is illustrated in Fig. 12.

Ridges and valleys are thus reflected quite clearly, to considerable depths.

It is quite clear from the diagrams that in homogeneous horizonta strata, topographic irregularities alone would give rise to irregularities of the isothermal contours. If topographic correction is applied when drawing these contours the representation is generally simplified and many anomalies disappear.

10. *Factor for Elevation with Respect to Sea Level.*—It is necessary in each district to measure the mean surface temperature at some particular well, preferably one liable to be least affected by rough topography in the neighbourhood. When this has been done the mean surface temperatures of other wells may be determined by adding or subtracting a correction which may, in dry climates, be as much as 5° F. per 1000 ft. difference of elevation. The exact figure must be determined for each region as it varies with the climate, being less in humid than in dry regions.

11. *Influence of Dip on Conductivity.*—In some sandstones, especially if micaceous, and in slates and some laminated shales, the conductivity perpendicular to the cleavage may be only about half that parallel to the cleavage, so that, in some districts, this additional factor must be allowed for.

12. *Some General Remarks on Static Thermal Fields.*—From what has been said regarding the static thermal state to be expected

in old structures, it is clear that in general no exact numerical relationship between the depths of thermal and structural contours will be obtainable, though fairly simple empirical relations valid over limited regions may be frequently observed and used to advantage.

The mathematical analysis of heat conduction in simple cases is often laborious but when complicated folds and unconformities are present and only the thermal properties of 50 or 60 ft. of exposed strata are well known, it becomes impossible to express, except in rough form, the thermal distribution in any area.

Fortunately, however, even approximate quantitative data, so long as the general disposition of the isogeotherms is given, are sufficient to be of great economic importance.

Another fortunate circumstance is the low average earth-gradient of about 1·0° C. per 10 ft., owing to which the minor irregularities due to thin beds of differing conductivity are masked on the depth temperature curves, and a particular bed must be a few hundred feet thick generally for a difference in its gradient to be noticeable.

An item urgently requiring attention is the question of gradients through thick beds of homogeneous strata, *e.g.*, thick oil, water or gas sands of various grades, carbonaceous, petroliferous, water-bearing, and barren limestones of different types, dry sands of various kinds, salt masses, saliferous shales, etc.

It is considered that this study would go far towards clearing up many of the geothermal questions.

Without a knowledge of a factor of primary importance, such as conductivity, it is useless to discuss items such as the possible influence of underground waters, hypothetical exothermic reactions in oil accumulations, or heat due to friction along active fault- and thrust-planes.

Only the residual anomalies left after accounting for varying conductivities and topography can be used as a basis for studying these other questions.

In particular the gradients through oil-bearing beds of various types require special study for comparison with the gradients through the same beds when not oil-bearing. Until the influence of the oil itself on conductivity has thus been measured in several fields, we shall not know the extent of the utility of geothermal methods in oilfields.

13. *Presentation of Geothermal Data.*—It will be evident from a consideration of the diagrams so far given that for the elucidation of geothermal data it is necessary to present the data in the form of isogeotherms drawn on a geological section, together with information regarding the lithology of the several beds.

For detailed work the depth-temperature curves for the several wells must also be shown, preferably along with the formations logged.

In taking well temperatures arbitrary and fairly wide spacing is frequently adopted; but the results would be of greater value if temperatures were taken especially at the top and bottom of such thick beds as might be supposed to cause irregularities in the flow of heat.

In some published reports on temperature investigations the results have been presented in the form either of contours drawn on an arbitrarily selected isothermal surface or on the depth to such a surface.

Such methods of presentation can scarcely be defended, as they give merely a minimum of information regarding the thermal distribution and none at all with respect to factors such as the nature and distribution of the rocks and their contents, surface irregularities, etc., on which it is obvious that the thermal field must depend.

In connection with recent work in the Tonkawa Cromwell fields isothermal contour maps have been published assuming an accuracy significant to 0·1° F. An examination of any set of depth temperature curves shows that anomalies considerably greater than this are of common occurrence, due to local conditions round a particular borehole, and the focussing of attention on such details with respect to one isothermal surface alone is likely to hinder progress more than aid it.

If the contours on other isothermal surfaces in this field are also inspected and compared, this point will be clear.

14. *Gradients and their Significance.*—In Prestwich's "Controverted Questions in Geology" and in Darton's "Geothermal Data of the United States," extensive lists of gradients have been assembled from temperature measurements in boreholes. A study of these lists shows wide variations in the values obtained, even in strata that might be expected to yield similar values. Nearly all these gradients have been calculated by subtracting the temperature at the bottom of the borehole from the mean surface temperature of the locality and dividing by the depth. It will be shown that from gradients calculated in this matter it is gener ally unsafe to make any deductions. Leaving out of account such circumstances as the influence of local waters and of chemical action, such as is known to occur in some metalliferous dep osits, the variation of gradient will be considered entirely from the poi nt of view of the effects due to conductivity.

In Fig. 1, for instance, suppose two boreholes No. 1 and No. be drilled in the positions shown and both reach the same depth

say, to the line AB., if the gradients for these two boreholes were calculated as indicated in the previous paragraph, no difference would be shown. If the boreholes were both shallower than this, No. 2, would show the lower gradient, and if both were deeper it would show the higher gradient. It is thus clear that detailed depth temperature curves are necessary and that the variation of the gradient with the depth is a most important consideration and this point should be kept in mind particularly when attempting to smooth out experimental depth temperature curves.

It should also be borne in mind that abnormally low gradients may be observed due simply to steep inclination of the isogeotherms so that it is only when sufficient observations have been made at closely spaced points to enable the isogeotherms to be drawn on a section, that one can have any definite idea of the true significance of the observed gradients, which, as we have seen, may vary greatly at different depths, in a particular well.

In extensive developments of horizontal strata, however, where the isogeotherms are sensibly horizontal and undisturbed the gradients at different depths in a particular well are of great importance in that they enable one to calculate with fair accuracy the relative conductivities of the several beds penetrated.

15. *Applications of Geothermal Methods to the study of Old Structures.*—In the case of rocks which are thermally isotropic, it is, in general, only when thick masses of appreciably different conductivity are associated that geothermal effects due to structure can be expected. Such rocks as rock salt, saliferous shales, coal-bearing beds and metallic ore-bodies differ most from average strata in their conductivity and it is with structure involving these beds that we should expect to obtain the most pronounced geothermal results. The most common types of structure have been dealt with in the previous pages and diagrams drawn showing the kinds of thermal fields to be expected.

The detailed application of these diagrams must be worked out in each district separately, having regard to local structural and lithological conditions and no general rules can be given for their use. Over a buried mass of coal-bearing beds for instance, covered by better conducting rocks, we should find depressed isogeotherms; further down the side of the mass the isogeotherms may have no sensible depression, whereas still further down the side of the mass, or inside it, we should soon come to abnormally high temperatures for the particular depth. From this it is clear that deductions cannot be made from the evidence of one borehole or mine shaft,

but that detailed observations from several are necessary if they are to be of practical use.

With regard to locating oil sands in a given structure by means of temperature we have at present insufficient data on the conductivity of oil bearing beds in comparison with the conductivity of the same beds when water logged or barren, and until these experimental data come to hand we must regard geothermal data as of use only in so far as they are indicative of structure.

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The International Committee for the Standardisation of Nomenclature and Tests of Road Materials.*

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The third meeting of the Committee was held on June 23rd, 1930, at Paris, with M. Lorieux as Chairman and Prof. P. Le Gavrian as Secretary.

There were present the representatives of France (Prof. Le Gavrian), Belgium (M. Van Volsom), Great Britain (Dr. P. E. Spielmann), Holland (Dr. F. J. Nellensteyn), Italy (Signor I. Vandone), Scandinavia (Mr. H. V. Rygner, Denmark), Spain (the Conde de Casa Rul). Switzerland (Prof. P. Schläpfer) and the United States of America (Mr. E. F. Kelly) were not represented personally.

A sympathetic reference was made to the death of Mr. Brodersen (Denmark).

The following matters were dealt with :—

1. *Technical Dictionary of Road Terms in Six Languages.*—This dictionary is expected to be published in a few months.

The scheme is arranged on a very simple and efficient plan. Each word, with its translation or definition, is given a reference number, and the entries in the Index in each of the six languages refer to these numbers, and not to pages. In this way, the original proposal to issue the dictionary in each of the six languages is avoided.

2. *Definitions.*—Owing to the fact that the Standardization of Tar Products Tests Committee, representing the Tar Industry of this country, was in a position to express its views on this matter only on a date later than that by which the International Committee had made its decisions, the matter was reopened only as an act of courtesy of the Council of the Association. This was done as a result of representations made by the Standardization of Tar Products Test Committee, through the British Engineering Standards Association to the Ministry of Transport, and through the Ministry to Paris.

At the same time that the new British proposals were being considered, new definitions put forward by the American Society for Testing Materials were also discussed. These had already been approved by three Committees of the A.S.T.M., namely :—

D–4, on Road and Paving Materials,

D–2, on Petroleum Products and Lubricants,

D–8, on Bituminous Waterproofing and Roofing Materials.

* Paper received August 15th, 1930.

It may be presumed that these new definitions were the result of the visit to Europe of Mr. Prevost Hubbard, who came to discuss the possibility of harmonising the significance to be attached to certain words.

The following definitions, existing and proposed, are indicated in Table I. :—

TABLE I.

Definitions, Existing and Proposed.

	International Committee.	British (S.P.T.P.C.).	U.S.A. (A.S.T.M.)
Bitumen—			
Existing	1	—	1
Proposed	—	—	2
Asphalt—			
Existing	3	—	4
Proposed	—	—	5
Tar—			
Existing	6	—	8
Proposed	—	7	9
Road tar—			
Existing	—	—	—
Proposed	—	10	—
Pitch—			
Existing	11	—	13
Proposed	—	12	14
Flux oil—			
Existing	—	—	—
Proposed	—	—	15

Bitumens.—1. All mixtures of natural or pyrogenic hydrocarbons and their non-metallic derivatives, whether gaseous, liquid, viscous or solid, that are entirely soluble in carbon disulphide.

2. Mixtures of hydrocarbons of natural or pyrogeneous origin or combinations of both (frequently accompanied by their non-metallic derivatives) which can be gaseous, liquid, semi-solid or solid and which are completely soluble in carbon disulphide.

Asphalt.—3. Natural or mechanical mixtures in which the asphaltic bitumen is associated with inert mineral matter.

The word "asphalt" is to be qualified by one indicating the origin of the product.

4. Solid or semi-solid native bitumens obtained by refining petroleum, or solid or semi-solid bitumens which are combinations of the bitumens mentioned with petroleums or derivatives thereof, which melt upon application of heat and which consist of a mixture of hydrocarbons and their derivatives of complex structure, largely cyclic and bridge compounds.

5. Black to dark brown solid or semi-solid materials which gradually liquefy when heated in which the predominating constituents are bitumens all of which occur in the solid or semi-solid

form in nature or are obtained by refining petroleums or which are combinations of the bitumens mentioned with each other or with petroleums or derivatives thereof.

Tar.—6. A product usually viscous; obtained by the condensation of volatile compounds evolved during the destructive distillation of the organic matter contained in coal (schist, shale) peat, vegetable matter, etc.

The word "tar" must always be preceded by the name of the material from which it is produced. Its mode of production should be also indicated.

7. A bituminous substance consisting substantially of the non-aqueous liquid condensate resulting from the destructive distillation of carbonaceous materials.

It is desirable that the derivation of the tar should be indicated.

8. Bitumens which yield pitches upon fractional distillation and which are produced as distillates by the destructive distillation of bitumens, pyrobitumens or organic matters. (A.S.T.M. Standard.)

9. Black to dark brown bituminous condensates, which yield substantial quantities of pitch when partially evaporated or fractionally distilled and which are produced by destructive distillation of organic material, such as coal, oil lignite, peat and wood.

Road tar.—10. A tar prepared to conform certain definite specifications.

Pitch.—11. The solid or semi-solid residue of the distillation of the tar.

12. The solid or semi-solid fusible residue remaining after removal by distillation of the several fractions from tar or tar products.

13. Solid residues produced by the evaporation or distillation of bitumens, the term being usually applied to residues obtained from tars. (A.S.T.M. Standard.)

14. Black or dark brown solid cementitious residues which gradually liquefy when heated and which are produced by the partial evaporation or fractional distillation of tars.

Fluxes.—15. Bituminous materials, generally liquid, in which the predominating constituent is bitumen, used in combination with asphalts for the purpose of softening the latter.

The decisions taken were the following:—

Bitumen.—The new American proposal was adopted in place of the existing International Committee's definition; the change was very small.

Asphalt.—The new American proposal was accepted as a U.S.A. definition, independent of the International Committee's definition It was felt that the two were still too divergent to be harmonised.

Tar.—The International Committee's definition has been modified to an important degree so as to conform to the British proposals for: (1) the inclusion of the word "bituminous"; (2) the exclusion of the crude aqueous distillate; and (3) the inferred inclusion of gas oil tar, by the removal of the enumeration of examples of tar from the definition proper to the note below it.

The Committee did not agree that tar was "a non-aqueous distillate," because, in fact, it did contain water (even though as an impurity), and also because the term "dehydrated tar" (included in the dictionary) showed that there was water present that could be removed.

Further, the Committee could not look upon Free Carbon as a "condensate," and therefore shortened and simplified the definition still further. Finally, the English phrase "carbonaceous materials" was decided to be the equivalent of "matieres organiques," the French language not having an exact equivalent.

The definition, as adopted, now has the final form :—

Tar.—A bituminous product, viscous or liquid, resulting from the destructive distillation of carbonaceous materials.

The word "tar" must always be preceded by the name of the material from which it is produced: coal, shale, peat, vegetable matter, etc.

Its mode of production should also be indicated.

Thus, except for "non-aqueous distillate," the British proposals have been accepted in effect, though not in verbal form.

Road tar.—After some discussion the significance and necessity for the British proposals were, at last, fully and sympathetically recognised, but the form was considered to be unsatisfactory as indicating no immediately obvious reason for its existence. It was also realised that materials other than tar might, in practice, have to be particularised in a similar manner. The whole position including that of road tar, has therefore been safeguarded by a Note inserted in the introduction of the dictionary to the effect that: certain materials having been defined in a general way, but it must be clearly understood that in some cases particular qualities of these materials, required for particular purposes, will have to conform to definite specifications.

Pitch.—The previous International Committee's definition was considered to cover also "Coke" in its wording. The new British proposals and the new American definition, being so close to one

another, a single new International definition has been produced from the two, which now runs as follows :—

"*Pitch.*—Black or dark brown, solid or semi-solid fusible and cementitious residue, remaining after partial evaporation or fractional distillation of tar or tar products."

Fluxes.—The new American definition has been accepted as an independent definition, as the Committee does not consider definition to be necessary.

3. *Tests.*—The comments of the various nations on the Questionnaire that had been circulated were considered, and the following decisions were taken :—

Viscosity.—The British tar viscometer has been adopted as the instrument for accurately measuring viscosity. The Hutchinson "Junior" tar tester has been accepted as being "useful" for employment "on the job"; and when this shows less than 3 seconds, then the (French) "E.P.C." instrument shall be used in its place : both instruments are considered as measuring "consistency." Further experience is invited.

Naphthalene determination.—An exact determination is not required. The methods of Schläpfer (Switzerland) and of Vandone (Italy) will be circulated.

Ductility.—No fundamental alteration to the Dow machine or conditions of test were recommended. Rygner (Denmark) uses the vertical machine of Abraham. Casa Rul (Spain) considers ductility, adhesion, and cohesion to be phenomena that should be studied together. His instrument, fundamentally rather resembling that of Kirschbaum, will be described and circulated. He finds that adhesivity is always greater than cohesivity.

Adhesivity.—No method of measurement was recommended. (See Casa Rul, above.)

Cohesivity.—Nellensteyn (Holland) considered this property to be connected with his "micron" and "ultra-micron" work. (See Casa Rul, above.)

Placticity.—Vandone (Italy) considered his method still to be lacking insufficient experience for it to be accepted for standardization. It is unsuitable for measuring the effect of static pressure.

Emulsions.—Mention was made of the importance of establishing conditions for the recovery of asphaltic bitumen in its original condition. The "Shell" method of analysis by means of acetone was referred to, and will be circulated. The (unratified) B.E.S.A. tests were referred to.

Stability.—Attention was drawn to the (unratified) B.E.S.A. tests; and Nellensteyn (Holland) will describe for circulation his method for measuring the time of break of emulsions as a test for their stability.

Paraffin wax.—The E.P.C. (H_2SO_4, approximate), the Marcusson, and the Schwartz methods of determination should be examined.

Presence of tar products.—Nellensteyn (Holland) considers Millon's reagent (mercuric nitrate) to be a satisfactory qualitative test.

Sampling.—The Paris office will correlate the British (S.T.P.T.C. and I.P.T.), American (A.S.T.M.) and Danish recommendations.

Atmospheric action.—It was recognised that the question, as put forward, was too comprehensive and complex. The committee asks for the study of

Variation of temperature,
Light,
Action of moisture,

as affecting road surfaces.

Paraffin wax content of asphaltic bitumen.—Method employed in the Chemical Laboratory of the Ecole des Ponts et Chaussées, Paris:—

1 to 1·5 g. of the sample are treated with 100 ml. of petroleum ether in an Erlenmeyer flask. After the separation of the asphaltenes, filtration is effected through a Gooch crucible.

The filtrate is transferred to a separating funnel, and 30 ml. of concentrated sulphuric acid are added. The mixture is shaken for three minutes, and then allowed to settle for about 20 hours.

The acid is then separated, and the remaining liquid is treated with an equal volume of concentrated sulphuric acid, and allowed to settle for several hours. The acid is then drawn off, and if strongly coloured the treatment is repeated.

The petroleum ether solution is first washed with distilled water, then with an aqueous 5 per cent. solution of potassium carbonate, and finally with distilled water. It is transferred to a crystallising dish of 8 cm. diameter and 5 cm. height. The petroleum ether is driven off on a water bath and in an air oven at 105° C.

The residue is taken up in a little ethyl ether and transferred into a flask, where an equal volume of absolute alcohol is added. The liquid is cooled to −20° C. by means of equal weights of snow and salt. Filtration is rapidly carried out under suction in a tared Gooch crucible, and the residue is washed with a mixture of equal volumes of alcohol and ethyl ether.

The crucible and its contents are dried at 105° C. and the weight of paraffin wax is calculated as a percentage on the original sample.

(*Translator's Note.*—The fundamental difference between this method and that of the I.P.T.—A.31, 1924, since withdrawn, is the preliminary separation of the asphaltenes.)

Further points that arose were :—

1. The British comment that the division of *tests* into *essential* and *useful* was a matter to be settled in specifications and contracts, and not by the International Committee, was not agreed to ; it was, on the contrary, held to be desirable to put before the less well informed the opinion of the Committee as to these two categories.

2. Rygner (Denmark) described the Hoepfner-Metzger method for the determination of the *solidification point* of tar or bitumen, by ascertaining the temperature—which may be as low as –40° C.—at which there is not more than 0·1 mm. penetration under standard conditions. It is, at present, more useful for the examination of tar-bitumen mixtures. It was accepted as " useful."

3. It was mentioned that *Germany* had recently become a member of the Permanent International Association of Road Congresses, and that representation on the International Committee was likely before long, to be considered.

CURRENT PETROLEUM NOTES.

U.S. Natural-Gasoline Industry, 1929.—The production of natural-gasoline in the United States in 1929 amounted to 2,233,688,000 gallons, an increase of 23 per cent. over 1928, and had a total value at the plants of $158,410,000.

The average yield of gasoline per 1000 cu. ft. of gas treated fell from 1·23 gal. in 1928 to 1·14 gal. in 1929, the first decline since 1924. The number of plants using the compression process dropped from 620 in 1928 to 442 in 1929, and the number of charcoal plants also declined from 27 to 23, but the absorption and combined absorption and compression or charcoal processes showed an increase.

Transport of natural-gasoline by pipe-line was stimulated by improvements in welding, and a line has recently been completed from Kettleman Hills to Avila, a distance of 88 miles.

Miscellaneous Petroleum Products, 1929.—The production of miscellaneous petroleum products in the United States in 1929, as compared with 1928, was as follows:—

	Thousands of Barrels.	
	1928.	1929.
Road Oils	2,972 ..	3,281
Refinery Gas	1,353 ..	1,884
Absorption Oils	269 ..	329
Petrolatum	312 ..	251
Furnace Oils	312 ..	215
Special Naphthas	117 ..	204
Medicinal Oils	87 ..	64
Other Products	3,980 ..	3,696
	9,402 ..	9,924

Deposition of Paraffin in Gas-Lift Wells.—The accumulation of paraffin in the eductor passage in gas-lift wells is a troublesome problem in California and generally results in the plugging of the upper part of the passage. In some cases the accumulations are removed by injecting steam with the input gas, and in others by heating the input gas to about 350° C. The application of these remedies is generally only necessary at about monthly intervals.

General information regarding gas-lift practice, with special reference to California, is given in U.S. Bureau of Mines Bulletin 323, obtainable from the Superintendent of Documents, Government Printing Office, Washington, D.C., price 30 cents.

Fatalities in California.—In 1929 there were 63 fatalities in the Californian petroleum industry as compared with 47 in 1928. This is the largest number since 1923 and coincided with a period of intensive development.

The refining and natural-gasoline divisions of the industry are exceptionally hazardous, and a study of safety precautions at natural-gasoline plants has recently been published by the U.S. Bureau of Mines. The Californian accidents are reviewed, and safety recommendations made, in the U.S. Bureau of Mines Report of Investigations 3041. Both these reports are obtainable from the U.S. Bureau of Mines, Dept. of Commerce, Washington, D.C.

ERRATUM.

Vol. 16. page 499. For $dH/dt = s = 0{\cdot}00090t - 0{\cdot}499$ (sp. gr.) $+ 0{\cdot}856$.
Read $dH/dt = s = 0{\cdot}00090t - 0{\cdot}477$ (sp. gr.) $+ 0{\cdot}856$.